

ORGANOGERMANIUM CHEMISTRY
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Received April 15, 1963

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I. INTRODUCTION

The chemistry of organic compounds of germanium was reviewed in 1951 by Johnson (91). This paper is intended as a supplement covering work done from the appearance of Johnson's article through 1962. It will not, however, include such compounds as the unsubstituted germanes and substituted germanes in which all substituents are purely inorganic, *e.g.*, halogen atoms or halogenoid groups. Compounds of these types were included in Johnson's article. The tables in section III give the physical constants and method of preparation of organogermanium compounds prepared since the appearance of Johnson's review. Compounds listed in that review are included only if better values

of the physical constants have been determined or if they are examples of a new method of synthesis. A section on spectra (section IV) has been added since much work on this subject has appeared in recent years.

Short general surveys of organogermanium chemistry are included in the monographs on organometallic chemistry by Coates (40a) and Rochow, Hurd, and Lewis (171a). A listing of the physical constants of some organogermanium compounds is given in Kaufman's Handbook (98a). A bibliography and review of the literature to June, 1960, has been published in Holland by Rijkens (169a); the physical constants of organogermanium compounds, however, are not included in that paper.

The major developments in organogermanium chem-

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istry since 1951 have been the preparation of organogermanium compounds containing unsaturated organic substituents, the study of the reactions of these compounds, especially polymerization, and the preparation of a series of compounds (the germirenes) in which the germanium atom is a member of a three-membered aromatic ring.

Interest in the study of organogermanium chemistry has been stimulated by the general question of the comparative properties of the Group IV elements, in particular, whether the electronegativity of germanium is greater than that of silicon (2, 45, 153, 170, 175, 188, 216).

II. GENERAL METHODS FOR THE SYNTHESIS OF ORGANOGERMANIUM COMPOUNDS

Of the six general methods listed by Johnson, all continue to be used. In addition to the older methods, A-F, four new general preparative methods have been introduced since 1951.

A. GRIGNARD REACTION

Reactions involving alkyl or aryl Grignard reagents continue as one of the main methods of organogermanium synthesis. A comparison of the preparation of tetraalkylgermanes by the Grignard and organolithium methods indicated that of the two the Grignard reaction gave the better yields (56).

Five- and six-membered ring systems with germanium in the ring have been prepared by reacting butyl and amyl di-Grignard reagents with germanium tetrachloride. A mixture of di- and tetrasubstituted products is obtained (127).

An attempt to prepare triethylgermane by the reaction of the ethyl Grignard reagent on trichlorogermane was unsuccessful; tetraethylgermane was the principal product (45).

In various reactions involving the introduction of additional alkyl groups into methylgermanium chlorides or methoxides, halogen interchange takes place along with, or even in preference to, substitution when the alkyl Grignard reagent is used. In the reaction between CH_3MgBr and $(\text{CH}_3)_2\text{GeCl}_2$, $(\text{CH}_3)_2\text{GeBr}_2$ was obtained in 25% yield, while the expected product, $(\text{CH}_3)_3\text{GeCl}$, was obtained in only 12% yield. Similarly $(\text{CH}_3)_3\text{GeCl}$ on reacting with CH_3MgBr gave $(\text{CH}_3)_3\text{GeBr}$ in 22% yield (162, 163). Dimethyldimethoxygermane reacts with methylmagnesium iodide to give trimethyliodo- rather than trimethylmethoxygermane (218). The ethyl Grignard reagent reacts with dimethyldichlorogermane to give equal amounts of $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{GeCl}$ and $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{GeBr}$ in low yield. Methylmagnesium iodide reacts with $(\text{CH}_3)(\text{CH}_2\text{Cl})\text{GeCl}_2$ to give $(\text{CH}_3)_3\text{GeCH}_2\text{I}$ (162, 163).

Treatment of GeCl_4 with the 1-naphthyl Grignard reagent results in the trisubstituted product only,

rather than the tetrasubstituted product, probably because of steric factors (215).

The mechanism of the formation of hexaaryldigermanes in the reaction of aryl Grignard reagents with GeCl_4 was studied by Glockling and Hooton (75). The reaction was shown to proceed by way of R_3GeMgX , formed through the reaction of the partially arylated intermediate, R_3GeX , with magnesium or with the Grignard reagent. The presence of R_3GeMgX in the reaction mixture was shown by the presence of R_3GeH among the products when a reaction which had not gone to completion was hydrolyzed.

Alkyl, aryl, or olefinic Grignard reagents react with mono- or dialkylgermanium hydrides in tetrahydrofuran (THF) upon long reflux (2-3 days) to give substitution at one of the hydrogen atoms (172).

Alkenyl Grignard Reactions

Allylmagnesium bromide is prepared by a normal Grignard reaction, and its use in the preparation of methyltrialkylgermane from methyltrichlorogermane shows no unusual features (159). The vinyl and *p*-vinylphenyl Grignard reagents, however, cannot be prepared by the usual methods. These reagents have only recently been successfully prepared in THF solution.

Normant's reagent, $\text{H}_2\text{C}=\text{CHMgBr}$, reacts with germanium tetrachloride in THF. After 20-hr. reflux, a mixture of the tetra vinyl (35%) and hexa vinyl (26%) compounds is obtained (188). Vinylmagnesium bromide has also been used to introduce vinyl groups into alkylgermanium halides (85, 99, 142, 156, 188).

Triethyl- and triphenylperfluorovinylgermane have been prepared by the reaction of R_3GeX , bromotrifluoroethylene and magnesium in a cooled THF solution for 12 hr. (192).

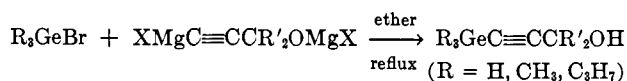
Leebrich and Ramsden's reagent, $\text{CH}_2=\text{CHC}_6\text{H}_4\text{-MgCl}$, has been used to introduce the *p*-vinylphenyl group into di- and trialkylgermanium compounds. This reaction requires 2-4 hr. heating at 50° in THF (145, 146, 155).

Acetylenic Grignard Reactions

Reaction of trialkylgermanium bromides with the acetylene mono-Grignard reagent requires 15 hr. stirring in THF solution. The substituted acetylenic Grignard reagents, $\text{RC}\equiv\text{CMgBr}$, which may be prepared in ether, add to alkylgermanium halides in a refluxing ether-benzene mixture. The 2-propynyl Grignard reagent, $\text{CH}\equiv\text{CCH}_2\text{MgBr}$, adds to alkylgermanium halides in ether (124, 125). Compounds of the type $\text{R}_3\text{GeC}\equiv\text{CGeR}_3$ (R = ethyl, phenyl, cyclohexyl) have been prepared by the reaction of organogermanium bromides with the acetylenic di-Grignard reagent (81).

Acetylenic alcohol groups may be introduced into organogermanium molecules by the use of Iotsich's

reagent (45, 203, 204)



Other Grignard Reactions

1,1'-Ferrocenylene di-Grignard reagent reacts with triphenylbromogermane in ether to give the monosubstituted compound, Fe(C₅H₅)[C₅H₄Ge(C₆H₅)₃], and a trace of the disubstituted compound (192).

B. ORGANOLITHIUM SYNTHESIS

No important modifications have been introduced since 1951 in the use of organolithium reagents for the preparation of symmetrical and unsymmetrical tetra-substituted germanes. Included among the reactions following the usual procedures are two in which organosilyllithium reagents are used. Germanium tetrachloride and trimethylchlorogermane react with the appropriate organosilyllithium reagent to give [(CH₃)₃-Si-*p*-C₆H₄]₄Ge (130) and (CH₃)₃Ge-*p*-C₆H₄CH₂Si(CH₃)₃ (47), respectively.

Schmidt and Ruidisch (180) compared four methods for the preparation of trimethylchlorogermane: reaction of the methyl Grignard reagent with GeCl₄, exchange between GeCl₄ and GeR₄, reaction of CH₃MgCl with (CH₃)₂GeCl₂ (for the difficulties involved in the use of CH₃MgBr for this purpose see the previous section), and the action of methyllithium on (CH₃)₂-GeCl₂. Of these only the latter two were successful, and the organolithium reaction gave the better yield. Only one case each of the use of an olefinic and acetylenic organolithium reagent has been reported; (C₆H₅)₃-GeCH₂CH=CH₂ (201) and (C₆H₅C≡C)₄Ge (24) have been prepared in this manner.

The reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene with organogermanium dihalides or with germanium tetrahalides results in a cyclopentadienyl structure with germanium in the ring. The dilithium reagent reacts with diphenylgermanium dihalide in ether to give hexaphenylgermole (109a) and with germanium tetrachloride to give octaphenyl-1,1'-spiro-digermole (109b). (See section III-L, for the structure of these compounds.)

Reactions Involving R₃M₂Li

Compounds of the type R₃MM'R₃, where M and M' are Group IV metals, have been prepared by the reaction of an alkali metal salt of one of the metals with a halide of the other metal. In this reaction the use of the lithium organometallic reagent, R₃M₂Li, differs little from that of the other alkali metals. Reactions of this type involving germanium are summarized in Table I.

Triphenylgermyllithium reacts with triethylperfluorovinylsilane in ethylene glycol dimethyl ether (GDME) at room temperature to give (C₆H₅)₃GeFC=CFSi-

TABLE I
COUPLING REACTIONS
R₃AM + R₃BX → R₄ABR₃ + MX

Reactant A	Reactant B	Solvent	Time of reaction, hr.	Yield, %	Reference
(C ₆ H ₅) ₃ SiLi	(C ₆ H ₅) ₃ GeCOOCH ₃	GDME	...	84	60
(C ₆ H ₅) ₃ SiK	(C ₆ H ₅) ₃ GeCl	Ether	1	43	64
(C ₆ H ₅) ₃ SiK	(C ₆ H ₅) ₃ GeBr	Ether	2.5	63	64
(C ₆ H ₅) ₃ GeLi	(C ₆ H ₅) ₃ SiCl	GDME	17	39.8	62
(C ₆ H ₅) ₃ GeLi	(C ₆ H ₅) ₃ SiCl	THF	...	52.5	57
(C ₆ H ₅) ₃ GeLi	(C ₆ H ₅) ₃ SnCl	Failed	66
(C ₆ H ₅) ₃ GeK	(C ₆ H ₅) ₃ SiCl	Ether	1	64.1	62
(C ₆ H ₅) ₃ GeK	(C ₆ H ₅) ₃ SnCl	Ether	17	60	66
(C ₆ H ₅) ₃ SnLi	(C ₆ H ₅) ₃ GeCl	Failed	66
[(C ₆ H ₅) ₃ Ge] ₂ SiLi	(C ₆ H ₅) ₃ SnCl	15.5	219

(C₂H₅)₃ (199). Triphenylgermyllithium also reacts with triphenylborane to form the salt Li[(C₆H₅)₃GeB(C₆H₅)₃]. The crude lithium salt thus formed is dissolved in methanol and precipitated with [(CH₃)₄N]⁺ or [(C₆H₅)₃P(CH₃)]⁺ (195).

C. WURTZ SYNTHESIS AND OTHER ALKALI METAL COUPLING REACTIONS

Coupling reactions involving sodium have been used since 1951 primarily to introduce an organic group R' into a molecule by reaction with a trisubstituted organogermanium halide (31, 47, 65). Two compounds in which an organosilicon group is introduced in this manner are (CH₃)₃Ge-*p*-CH₂C₆H₄Si(CH₃)₃ (25) and (C₂H₅)₃Ge-*p*-C₆H₄OSi(CH₃)₃ (47).

Potassium and lithium have been used in several coupling reactions. Those coupling reactions which involve the preparation of compounds with M-M' bonds are listed in Table I. Brown and Fowles (33) prepared (CH₃)₆Ge₂ by the reaction of (CH₃)₃GeCl with potassium under vacuum. Tribromophenylgermane and dibromodiphenylgermane react with lithium amalgam in ether under nitrogen atmosphere to give 1,1,2,2-tetrabromodiphenyldigermene and 1,2-dibromotetraphenyldigermene, respectively (133).

Tetrastrylgermane has been prepared by reacting C₆H₅CH=CHCl and GeCl₄ with sodium in refluxing benzene for 17 hr. A small amount of the hexastyryl compound (C₆H₅CH=CH)₆Ge₂ (0.5%) was produced as a by-product of this reaction (24).

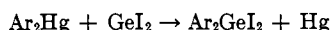
Bis-(triphenylgermyl)-diacetylene, (C₆H₅)₃GeC≡C-C≡CGe(C₆H₅)₃, has been prepared in two ways: by the reaction of triphenylgermanium bromide with disodium diacetylide in THF, and by the reaction of sodium triphenylgermanide with diiodoacetylene in ether (82).

1,1'-Ferrocenylenedisodium reacts with triphenylbromogermane in refluxing pentane to give triphenylgermylferrocene, Fe(C₅H₅)[C₅H₄Ge(C₆H₅)₃] (10%), and 1,1'-bis-(triphenylgermyl)-ferrocene, Fe[C₅H₄Ge(C₆H₅)₃]₂ (38%) (192).

D. ORGANOMERCURY SYNTHESIS

Equimolar amounts of GeI₂ and diarylmercury react in refluxing toluene to give a mixture of RGeI₃, R₂GeI₂

(the main product, 40–70% yield), and $R_3\text{GeI}$. Separation of the products of this reaction is often made easier by conversion of the iodides to oxides. The primary reaction is presumably



The tetrasubstituted germane was not obtained from this reaction, nor was it obtained from the reaction between $(m\text{-CH}_3\text{C}_6\text{H}_4)_3\text{GeI}$ and $(m\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Hg}$ (52).

Brinckman and Stone (29) prepared vinyltrichlorogermane in 67% yield by the reaction of vinylmercury with germanium tetrachloride.

The reaction between di-*n*-butylmercury and GeI_2 in acetone solution gives a solid product, with analysis corresponding to $(n\text{-C}_4\text{H}_9)_2\text{GeI-GeI}(n\text{-C}_4\text{H}_9)_2$ (90).

E. DIRECT SYNTHESIS

The preparation of methyl and ethyl germanium halides by the reaction of the organic halides with a germanium-copper mixture has been discussed in Johnson's review (91). Rochow, Didschenko, and West (171) investigated the preparation of *n*-propylgermanium chlorides in order to determine if the high reaction temperatures (310–330°) would cause isomerization. No isopropyl compounds were found. In this reaction, unlike the earlier preparations, the predominant product was the mono- rather than the dialkyl compound.

The direct synthesis of methylgermanium chlorides has been reinvestigated in order to study the conditions governing the relative proportions of mono- and dimethyl compounds formed. It was found that the formation of methylgermanium trichloride was favored by higher temperatures (*ca.* 550°) and an increased proportion of copper in the mixture (159, 162).

Petrov, Mironov, and Golgy (159) prepared the first unsaturated organogermanium compounds, allyltrichlorogermane and 2-methylallyltrichlorogermane, by direct synthesis using the usual procedures.

F. ZINC DIALKYL SYNTHESIS

This method proved to be more suitable for the preparation of a very pure, small sample of tetramethylgermane than the Grignard synthesis. Zinc dimethyl and germanium tetrachloride were mixed at -78° and gradually heated to 0° . Tetramethylgermane was obtained in 100% yield (111).

G. ADDITION OF GERMANIUM HYDRIDES TO DOUBLE AND TRIPLE BONDS

The addition of HSiCl_3 to olefins using free radical catalysts is a well known reaction. Fischer, West, and Rochow (53) successfully added HGeCl_3 to the double bond in 1-hexene obtaining hexyltrichlorogermane in 22% yield. The conditions used were those previously established for the HSiCl_3 addition, namely, refluxing at 60–64° for 35 hr. in the presence of benzoyl

peroxide. Under the same conditions, HGeCl_3 was successfully added to several olefins (168) and triphenylgermane to 1-octene (54), triphenylallylgermane, and 1-octadecene (65). Gilman and Gerow (67) demonstrated that with triphenylgermane the addition was at the terminal carbon of the olefin.

Lesbre and Satge (115) found that addition of trialkylgermanes to allyl alcohol and acrolein requires the presence of a peroxide catalyst, whereas addition to acrylonitrile or acrylic acid proceeds under reflux without catalysis.

Ponomarenko and Vzenkova (162) have shown that HGeCl_3 adds exothermically to olefins at room temperature without catalysts. The yields for the uncatalyzed addition are generally higher than those previously reported for the catalyzed addition. The addition to acetylene gives the double addition product $\text{Cl}_3\text{GeCH}_2\text{-CH}_2\text{GeCl}_3$.

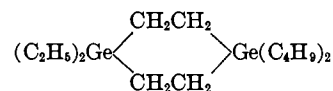
The addition of HGeCl_3 to vinyl chloride without catalyst gives the β addition product $\text{Cl}_3\text{GeCH}_2\text{CH}_2\text{Cl}$, in high yield, in contrast to the corresponding HSiCl_3 addition which gives only the α product and in low yield. Addition of HGeCl_3 to more highly chlorinated ethylene derivatives requires higher temperatures (138). Trichlorogermane adds to cyclopentadiene exothermically to give cyclopentenyltrichlorogermane and to cyclopentene upon reflux to give cyclopentyltrichlorogermane (141).

Trialkylgermanium hydrides add to substituted acetylenes generally giving a mono-addition product, $\text{R}_3\text{GeCH=CHR}'$. This reaction requires chloroplatinic acid catalyst. Where R is C_6H_5 or $n\text{-C}_4\text{H}_9$, the reaction is exothermic; in other reactions reflux conditions are necessary (45, 116, 124).

Triphenylgermane adds without catalyst to substituted olefins of the type $\text{CH}_2=\text{CHY}$ where Y contains a functional group terminal to the double bond or conjugated with it. Reaction times vary from 4 hr. to 5 days, with reflux (84).

Triphenylgermane adds in the presence of benzoyl peroxide to allyltriphenylsilane (131) and allyltriphenylgermane (65), but not to allyltriphenylstannane (59); nor does triphenylstannane add to allyltriphenylgermane (87).

Addition of dialkylgermanium hydrides to olefins containing functional groups results in a mixture of mono- and disubstituted products (172). *n*-Heptylgermane, $n\text{-C}_7\text{H}_{15}\text{GeH}_3$, adds to 1-heptene (114) and vinyl butyl ether (172) to give the trisubstituted product $n\text{-C}_7\text{H}_{15}\text{Ge}(\text{CH}_2\text{CH}_2\text{R})_3$. Dibutylgermane adds to diethyldivinylgermane to give both a cyclic product



and a polymeric material (127).

H. ALKYLALUMINUM SYNTHESIS

Tetraethylgermane (97, 220) and tetraisobutylgermane (220) have been prepared by heating germanium tetrachloride with trialkylaluminum (6 hr. at 110–130°).

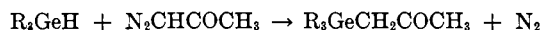
I. DIAZO ADDITION REACTIONS

Under this heading are grouped three separate reactions of diazo or diazonium compounds by which an organic group can be bonded to germanium.

Seyferth and Rochow (197) found that germanium tetrachloride and methyltrichlorogermane react with diazomethane in ether, cooled to -60° , to give $\text{CH}_2\text{-ClGeCl}_3$ and $(\text{CH}_3)(\text{CH}_2\text{Cl})\text{GeCl}_2$, respectively. An excess of diazomethane results in a mixture of mono-substituted and disubstituted products. Diazomethane does not react with dimethyldichlorogermane.

Aryl diazonium fluoroborates react exothermically with a mixture of zinc dust and germanium tetrachloride in an acetone solution cooled to -8° to give the mono-arylgermanium compound. Benzene diazonium fluoroborate after hydrolysis of the reaction products gives $(\text{C}_6\text{H}_5\text{GeO})_2\text{O}$ in 27% yield. With other aryl groups the yields are much lower (144).

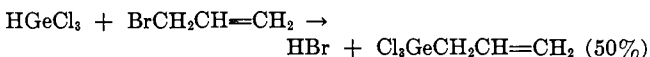
Trialkylgermanium hydrides react with ethyl diazoacetate, $\text{N}_2\text{CHCOOC}_2\text{H}_5$, diazoacetone, $\text{N}_2\text{CHCOCH}_3$, and diazoacetophenone, $\text{N}_2\text{CHCOC}_6\text{H}_5$, in refluxing benzene or toluene with copper catalyst



Yields of 30–40% are obtained. This reaction is useful for obtaining compounds with functional groups β to the germanium atom (115, 172).

J. CONDENSATION OF GERMANIUM HYDRIDES WITH ORGANIC HALIDES

Trichlorogermane, instead of adding to the double bond in allyl bromide, undergoes a condensation reaction (137)



The hydrogen bromide formed in this reaction reacts with part of the allyltrichlorogermane to give allyltribromogermane in 9% yield. Allyl iodide and methallyl bromide react with trichlorogermane in the same manner giving allyltrichlorogermane and methallyltrichlorogermane, respectively, as the only products. With allyl chloride and methallyl chloride, however, the condensation reaction takes place only in the presence of ether; without ether, addition occurs. With these two compounds, both addition and condensation may take place on the same molecule. Thus with allyl chloride the product of the condensation reaction is obtained in 27% yield, while $\text{Cl}_3\text{GeCH}_2\text{CH}(\text{CH}_2\text{Cl})\text{-GeCl}_3$ is obtained in 57% yield. Similarly with methallyl chloride both methallyltrichlorogermane

(58%) and $\text{Cl}_3\text{GeCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{GeCl}_3$ (11%) are obtained (136).

Triethylgermane, in the presence of chloroplatinic acid, gives somewhat the same reaction, but the situation is complicated by the fact that a halogenation reaction also takes place. With allyl bromide and iodide a mixture of triethylgermanium halide (*ca.* 50%) and allyltrichlorogermane (*ca.* 30%) is obtained. With allyl chloride there are three reactions: halogenation (55%), condensation (26%), and addition (5%). Methallyl chloride does not give the condensation reaction with triethylgermane (136).

This reaction has not been found to be generally applicable to alkyl and aryl halides; trichlorogermane, however, does undergo the condensation reaction with benzyl chloride and *t*-butyl chloride (136).

Trichlorogermane condenses with *p*-dichlorobenzene when heated to 550° resulting in *p*- $\text{ClC}_6\text{H}_4\text{GeCl}_3$. An attempted condensation of HGeCl_3 with chlorobenzene resulted in only a trace of phenyltrichlorogermane (204a).

III. CHEMISTRY OF ORGANOGERMANIUM COMPOUNDS

A. ALKYL- AND ARYLGERMANES

Preparative Methods

The following general methods for preparing compounds of the type R_4Ge , or for introducing a group R' into a molecule, have been discussed more fully in section II or in Johnson's article (91).

1. Grignard reaction.
2. Organolithium synthesis.
3. Wurtz synthesis.
4. Addition of a hydride to a double bond.
5. Alkyl aluminum synthesis.
6. Reactions with diazonium compounds.
7. Zinc dialkyl synthesis.

The following methods were used for the introduction of a group R' into a molecule.

8. Addition of R_3GeM to a double bond. A suspension of triphenylgermyllithium adds to the double bond in 1,1-diphenylethene, octadecene, and benzylacetophenone upon stirring overnight, with yields of the order of 10–25%. Similarly an ether suspension of triphenylgermylpotassium adds to the double bond of 1,1-diphenylethene. Under the same conditions, however, $(\text{C}_6\text{H}_5)_3\text{GeLi}$ does not add to 1-octene, *trans*-stilbene, or cyclohexene (65).

9. Other reactions of R_3GeM with a functional group. A suspension of triphenylgermyllithium in GDME will add to formaldehyde to give $(\text{C}_6\text{H}_5)_3\text{-GeCH}_2\text{OH}$, to benzophenone to give $(\text{C}_6\text{H}_5)_2\text{GeC(OH)-}$ (C_6H_5)₂ (61), and to tetrahydrofuran to give $(\text{C}_6\text{H}_5)_3\text{-GeC}_4\text{H}_8\text{OH}$ (72). These reactions have yields of the

order of 25–35%. Triphenylgermanium magnesium chloride is formed only in tetrahydrofuran solution and reacts with the solvent immediately to give $(C_6H_5)_3GeC_4H_9OH$ in 83% yield (72).

The following methods have been used for introducing or changing functional groups on side chains of organo-germanium molecules.

10. Reactions of Grignard reagents at side chains. Triphenylgermane carboxylic acid or its methyl ester reacts with the phenyl Grignard reagent or phenyllithium in ether solution to form the compound $(C_6H_5)_3GeC(OH)(C_6H_5)_2$ (61). The triethylgermyl-phenyl Grignard reagent, $(C_2H_5)_3GeC_6H_4MgBr$, reacts with acetaldehyde to form $(C_2H_5)_3GeC_6H_4CH(OH)CH_3$ and with ethylene oxide to form $(C_2H_5)_3GeC_6H_4CH_2CH_2OH$. These reactions require extensive reflux time (2–5 days) in ether solution and give rather low yields (99).

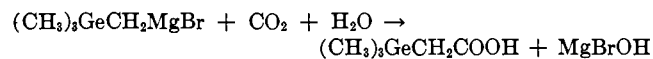
11. Addition to a side chain double bond. The SH group in $SHCH_2CH_2OH$ and $SHCH_2COOH$ and the Ge–H group in $(C_2H_5)_3GeH$ add to substituent double bonds without a catalyst. Water adds in the presence of $KMnO_4$, while $CHCl_3$ and $CH_2BrCOOC_2H_5$ add with benzoyl peroxide as a catalyst. Hydrogen bromide adds to a substituent vinyl group but attempted addition to a substituent allyl group results in cleavage of the Ge–C bond. Iodine and $CH_2BrCOOC_2H_5$ also cleave the Ge–C bond (128).

12. Trimethylvinylgermane reacts with iodomethylzinc iodide, ICH_2ZnI , in refluxing ether to give triethylcyclopropylgermane in 29% yield (190).

13. Potassium permanganate oxidizes $(C_6H_5)_3Ge-m-C_6H_4CH_2OH$ to give $(C_6H_5)_3Ge-m-C_6H_4COOH$ in 55% yield (22).

14. Chromium trioxide oxidizes $(C_6H_5)_3Ge-m-C_6H_4CH_3$ in a solution of concentrated sulfuric–acetic acids to the corresponding *m*-benzoic acid. The yield is considerably lower (10%) than the preceding oxidation (22).

15. The carboxylation of a Grignard reagent or organolithium reagent results in a substituent carboxyl group, *e.g.*



Yields are comparable to or higher than permanganate oxidation (22, 25, 31, 38).

16. The *m*- and *p*-nitro derivatives, $(C_2H_5)_3GeC_6H_4NO_2$, were prepared by the cleavage of the corresponding $(C_2H_5)_3GeC_6H_4Ge(C_2H_5)_3$ compounds using a solution of HNO_3 in acetic acid and refluxing for 6 hr. (46).

17. Lithium aluminum hydride can be used to reduce a substituent carboxylic group to an alcohol (61, 172) or a cyano group to an amine (172). Although the reactions are initially exothermic, reflux times of 4–10 hr. are necessary for completion.

Properties

The chemical properties of the tetraalkyl and tetraaryl germanes listed in Table III are in general the same as those described by Johnson (91). An exception is $(C_6H_5)_3GeCH(OH)(C_6H_5)_2$ which is unstable to air, undergoing a slow oxidation (61).

The spectra of the cyclopentadienyl derivatives, $(C_2H_5)_3GeC_5H_5$ and $(CH_3)_2Ge(C_5H_5)_2$, indicate that the bonding is covalent and that these are not metallocene compounds (141).

Several studies have been made of the ability of various reagents to cleave the Ge–C bond in tetraalkyl and tetraaryl germanes and the Ge–Ge bond in digermanes. The results of these studies are given in Table II. In several of these reactions the starting material was not recovered, indicating that cleavage had taken place, but no characterizable derivatives were obtained, indicating that some further reaction had taken place, perhaps with the solvent (68, 88a).

Bromine cleaves diphenylgermanocyclopentane at the phenyl group, but with diethylgermanocyclopentane the ring is completely split out leaving dibromodiethylgermane. Sulfuric acid opens the ring with both diethylgermanocyclopentane and diethylgermanocyclohexane (127).

The rates of cleavage of the aryl–metal bonds in compounds of the type R_3MAr where M represents a Group IVb metal have been measured in aqueous ethanolic perchloric acid. The rates are found to follow the sequence: Si 1, Ge 36, Sn 3.5×10^{-5} , Pb 2.0×10^{-8} ; this sequence does not seem to be related to electronegativity (48).

The acid strength of *p*-trimethylgermylmethylbenzoic acid is weaker than its silicon analog; a result which has been interpreted as being consistent with the greater electronegativity of silicon. The rate of cleavage of *p*- $(CH_3)_3GeCH_2C_6H_4Si(CH_3)_3$ as compared with *p*- $(CH_3)_3SiCH_2C_6H_4Si(CH_3)_3$ is also consistent with this interpretation. The greater strength of trimethylgermylacetic acid as compared with its silicon analog is, according to this theory, due to steric factors (25).

The presence of dative bonding between the metal ion and the aromatic ring in the phenyl compounds of Group IV elements has been studied through its effects on the reactions of compounds of the type $(C_6H_5)_3MC_6H_4X$. The existence of such bonding has been shown, and the effect is found to be approximately equal in silicon, germanium, and tin (22, 25).

The cleavage of various aryl triethylgermanes in aqueous–methanolic perchloric acid (49), and in an acetic–sulfuric acid mixture (50) was studied to determine the effect of various substituents on the aryl group in electrophilic aromatic substitution reactions.

The heat of combustion of tetraphenylgermane has been determined calorimetrically. Using the value

TABLE II
 CLEAVAGE OF ALKYL AND ARYL GERMANES

Compound	Cleavage agent	Solvent	Starting material recovered, %	Derivative obtained, %	References	
(C ₂ H ₅) ₄ Ge	Lithium	GDME (25°)	72	...	68	
		(80°)	35	...		
		(80°) ^a	70	...		
	Na/K alloy	Xylene		
		Diethyl ether		
		Diethyl ether ^a		
		GDME		
		GDME ^a		
		Di- <i>n</i> -butyl ether		
		Benzene		
		Xylene		
		Dioxane		
		Triethylamine		
		THF		
(C ₄ H ₉) ₄ Ge	Lithium	GDME	92	...	68	
Na/K alloy	GDME	100	...			
(C ₈ H ₁₇) ₄ Ge	Lithium	GDME	67	...	68	
(C ₆ H ₁₃) ₃ GeC ₆ H ₅	Lithium	GDME	65	...	68	
(CH ₃) ₆ Ge ₂	Na/K alloy	GDME	44	...	33	
(C ₆ H ₅ CH ₂) ₄ Ge	Lithium	GDME	100	...	68	
(2-C ₆ H ₅ C ₂ H ₄) ₄ Ge	Lithium	GDME	100	...	68	
(C ₆ H ₅) ₄ Ge	Lithium	GDME	...	70	60	
(C ₆ H ₅) ₃ Ge- <i>n</i> -C ₈ H ₁₇	Lithium	GDME	21	17.6	68	
(C ₆ H ₅) ₃ GeC ₂ H ₄ C ₆ H ₅	Lithium	GDME	67	28.6	68	
(C ₆ H ₅) ₃ GeC(C ₆ H ₅) ₃	Na/K alloy	Diethyl ether	8	74	31	
		Iodine	Xylene, refluxing	90		...
		CCl ₄ , refluxing	98	...		
	(C ₆ H ₅) ₆ Ge ₂	Oxygen	Xylene, refluxing	90	...	31, 62, 210
		Na/K alloy	Diethyl ether	96	...	
			Di- <i>n</i> -butyl ether	...	Oil	
			Xylene, refluxing	...	Oil	
			THF	
			Diethyl ether ^a	...	83	
			Benzene ^a	76.7	...	
GDME	64.0	24.7				
Cesium	Phenyllithium	Diethyl ether	50.0	...		
		Diethyl ether	81.0	...		
	Sodium	Xylene, refluxing	94.0	...		
		Xylene, refluxing	40.0	Oil		
	Potassium	GDME	38.0	...		
		Benzene, refluxing	90.0	...		
	Lithium	GDME	...	38.9		
		THF	...	75		
	Iodine	CCl ₄ , refluxing	100	...		
		Xylene, refluxing	40.0	9.7		

^a Initiator used; THF, tetraphenylgermane, or bromobenzene.

obtained, the heat of formation and the dissociation energy have been calculated. The dissociation energy of the Ge-C_{ar} bond was found to be 32.2 kcal./mole (23).

B. ORGANOGERMANIUM HYDRIDES

Preparation

Organogermanium hydrides have been prepared primarily by the reduction of chlorides, oxides, or sulfides using a variety of reagents.

1. Reduction using sodium in liquid ammonia.
2. Reduction using lithium aluminum hydride. These methods are discussed fully in Johnson's review

(91). The lithium aluminum hydride reduction has become the standard method.

3. Reduction using Zn-HCl. Germanium halides, unlike those of silicon and tin, are reduced to the hydrides by zinc in hydrochloric acid. Yields are extremely low; the method is, therefore, of little practical value (216).

4. Reduction using sodium borohydride (172).

5. Reduction using lithium hydride (163, 164). These reactions are carried out in the same manner as the lithium aluminum hydride reaction, with similar or slightly lower yields (70-90%). The solvent for

TABLE III
 ALKYL AND ARYL GERMANES

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
A. Tetrasubstituted symmetrical germanes							
(CH ₃) ₄ Ge	43.2 (736)		1.3863 (25)	0.9661 (25)	7	100	110, 218
(C ₂ H ₅) ₄ Ge	163.5 (760)	-92.7	1.4430	.9932	1	95	74
(<i>n</i> -C ₄ H ₉) ₄ Ge	278 (760)		1.4571	.934	5	72.9	220
(<i>i</i> -C ₄ H ₉) ₄ Ge	135 (17)		1.4580	.9364	1	80	7
(<i>n</i> -C ₆ H ₁₃) ₄ Ge	158-161 (760)		1.4567 (27)	.908 (27)	5	73.1	112, 220
(<i>n</i> -C ₇ H ₁₅) ₄ Ge	217 (3)		1.4626	.8985	2	14	55
(<i>n</i> -C ₈ H ₁₇) ₄ Ge	236 (2)		1.4640	.8938	1		114
					2	21.3	56
					1		114
(<i>n</i> -C ₁₀ H ₂₁) ₄ Ge	230-240 (0.015)		1.4643 (25)	.879 (31)	2	18	56
(<i>n</i> -C ₁₂ H ₂₅) ₄ Ge	330-340 (0.0005)		1.4654 (31)	.879 (31)	1	47	56
(<i>n</i> -C ₁₄ H ₂₉) ₄ Ge	360-370 (0.0005)		1.4640 (31)	.880 (31)	1	37.6	56
(<i>n</i> -C ₁₆ H ₃₃) ₄ Ge		37-38			1	36	56
(<i>n</i> -C ₁₈ H ₃₇) ₄ Ge		43-45			1	24	56
(2-C ₂ H ₅ C ₆ H ₁₁) ₄ Ge	193-196.5 (0.15)		1.4688 (24)	.909 (26)	2	27	56
(2-C ₆ H ₁₁ C ₂ H ₅) ₄ Ge		137.5-138.5			2	5	56
(2-C ₆ H ₅ C ₂ H ₅) ₄ Ge		53-54			1	21.6	56
(3-C ₆ H ₅ C ₃ H ₇) ₄ Ge	240-250 (0.05)		1.5704	1.106 (25)	2	33	56
(C ₆ H ₇) ₄ Ge		196-198			1		113
(1-C ₁₀ H ₇) ₄ Ge		270			2	38	215
(C ₄ H ₉) ₂ Ge ^a	188-189 (760)		1.5118	1.1837	1		127
(C ₈ H ₁₀) ₂ Ge ^b	108-109 (17)		1.5060	1.1140	1		127
B. Unsymmetrical tetrasubstituted germanes							
(CH ₃) ₃ GeC ₂ H ₅	79-80 (760)		1.4090	0.9843	1		112
(CH ₃) ₂ GeC ₃ H ₇		1.4331 (25)			12		190
(CH ₃) ₂ GeC ₆ H ₅	32 (9)		1.4697	1.5210	4	75	141
(CH ₃) ₂ GeC ₈ H ₉	34.5 (8)		1.4552	1.0422	1	94	141
(CH ₃) ₂ GeCH ₂ C ₆ H ₅	94-95 (28)		1.5140	1.1011	1		136
(CH ₃) ₂ Ge(C ₂ H ₅) ₂	108-109 (760)		1.4221	0.9885	1		112
(CH ₃) ₂ Ge(C ₆ H ₅) ₂	71-73 (4)		1.5490	1.4629	1	31	141
(C ₂ H ₅) ₃ Ge(CH ₃)	135 (760)		1.4332	0.9906	1		112
(C ₂ H ₅) ₃ Ge- <i>n</i> -C ₆ H ₇	73-74 (20)		1.4660	.9810	1		112
(C ₂ H ₅) ₃ Ge- <i>n</i> -C ₄ H ₉	180-181.5 (760)		1.4475	.9711	2	57.1	68
					1		112
(C ₂ H ₅) ₃ Ge- <i>n</i> -C ₆ H ₁₁	104-105 (20)		1.4495	.9625	2		112
(C ₂ H ₅) ₃ GeC ₆ H ₅	105 (16)		1.5029	1.0740	1	67	113, 141
(C ₂ H ₅) ₃ GeC ₈ H ₉	133 (40)		1.4756	1.0343	11		113
(C ₂ H ₅) ₃ Ge- <i>p</i> -C ₆ H ₄ CH ₃	136 (16)		1.5134		1	65	47
(C ₂ H ₅) ₃ Ge- <i>o</i> -C ₆ H ₄ CH ₃	126 (11)		1.5200		3	74	47
(C ₂ H ₅) ₃ Ge- <i>m</i> -C ₆ H ₄ CH ₃	128 (12)		1.5140		3	63	47
(C ₂ H ₅) ₃ Ge- <i>p</i> -C ₆ H ₄ - <i>i</i> -C ₂ H ₇	136 (7)		1.5095		1	70	47
(C ₂ H ₅) ₃ Ge- <i>m</i> -C ₆ H ₄ - <i>t</i> -C ₄ H ₉	116-117 (4-5)		1.5050		2	92	47
(C ₂ H ₅) ₃ Ge-2-, 4-, 6-C ₆ H ₂ (CH ₃) ₂	152 (9)		1.5333		2	90	47
(C ₂ H ₅) ₃ Ge- <i>p</i> -C ₆ H ₄ - <i>t</i> -C ₄ H ₉	125 (2)		1.5105		1	85	47
(C ₂ H ₅) ₃ GeCH ₂ C ₆ H ₅	78-81 (1)		1.5178		2	79	68
(C ₂ H ₅) ₃ Ge- <i>o</i> -C ₆ H ₄ C ₆ H ₅	159 (3)		1.5701		3	55	47
					2	62.4	68
(C ₂ H ₅) ₃ Ge- <i>p</i> -C ₆ H ₄ C ₆ H ₅	158-159 (0.7)		1.5080		2	87	47
(C ₂ H ₅) ₃ GeC ₈ H ₉	161 (4)		1.5589	1.230	1		113
(C ₂ H ₅) ₂ GeCH(C ₆ H ₄) ₂	165 (0.5)		1.6071	1.761	1		113
(C ₂ H ₅) ₂ Ge-1-C ₁₀ H ₇	153 (4)		1.5120		3	25	47
(C ₂ H ₅) ₂ Ge-2-C ₁₀ H ₇	153 (3-4)		1.5785		3	64	47
(<i>n</i> -C ₄ H ₉) ₂ Ge(C ₂ H ₅) ₂	109-110 (14)		1.4516	0.9547	1		112
(<i>n</i> -C ₄ H ₉) ₂ GeC ₆ H ₅	109 (0.4)		1.4942	1.0115	1		113
(<i>n</i> -C ₅ H ₁₁) ₂ GeC ₂ H ₅	148-149 (7)		1.4565	0.9274	1		112
(<i>n</i> -C ₆ H ₁₃) ₂ GeC ₆ H ₅	160-165 (760)		1.4984 (22)	.972 (25)	2	75	55
(C ₆ H ₁₁) ₂ Ge- <i>p</i> -C ₆ H ₄ CH ₃		135			2	86	47
(C ₆ H ₁₁) ₂ Ge- <i>m</i> -C ₆ H ₄ CH ₃		124			2	90	47
(C ₆ H ₁₁) ₂ Ge- <i>p</i> -C ₆ H ₄ C ₂ H ₅		138			2	40	47
(C ₆ H ₁₁) ₂ Ge- <i>p</i> -C ₆ H ₄ - <i>i</i> -C ₂ H ₇		129.5			2	80	47
(C ₆ H ₁₁) ₂ Ge- <i>p</i> -C ₆ H ₄ - <i>t</i> -C ₄ H ₉		159.5			2	87	47

TABLE III (Continued)

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
$(C_6H_5)_3GeC_3H_5$		72-73			2	62	54
					4	91	54, 84
$(C_6H_5)_3GeC_{13}H_{27}$		76.5-77.5			2	70	68
					4	67	65, 84
					8	27.3	65
					1	30	65
$(C_6H_5)_3GeC_6H_{11}$		144-147			1	31	54
					4	39	54, 84
$(C_6H_5)_3GeC_5H_9$		176-177			1		113
$(C_6H_5)_3GeCH_2CH_2C_6H_5$		145-146			4	40	84
					2	70.6	68
$(C_6H_5)_3GeCH_2CH(C_6H_5)_2$		96-97			8	15	65
					3	9	65
$(C_6H_5)_3GeC_6H_4CH(C_6H_5)_2$		208-210			1	65	31
$(C_6H_5)_3GeC(C_6H_5)_3$		342-344			3	57	31
$(C_6H_5)_3GeC_3H_7$		126			1		113
$(C_6H_5)_3GeCH(C_6H_5)_2$		214			1		113
$(C_6H_5)_2Ge(CH_2CH_2C_6H_5)(C_{13}H_{27})$		34.5-35.5			2	28.6	68
$(C_6H_5)_2Ge(C_9H_{17})_2$		144-145			1		113
$C_4H_8Ge(C_2H_5)_2^a$	173-174 (750)		1.4725	1.1140	1	86	127
$C_4H_8Ge(C_4H_9)_2^a$	115 (0.2)	33	1.5971	1.1218	1	83	127
$C_4H_8GeC_5H_{10}^b$	101 (23)		1.5058	1.1474	1	45	127
$C_5H_{10}Ge(C_2H_5)_2^c$	116-117 (72)		1.4742	1.0663	1	87	127
$C_5H_{10}Ge(C_2H_5)_2^c$	150 (1)		1.5932	1.2061	1	79	127
C. Compounds of the type $R_3GeRGeR_3$							
$(CH_3)_3GeCH_2CH_2CH_2Ge(CH_3)_3$	90 (28)		1.4500	1.1075	1	72	136
$(C_2H_5)_3Ge(CH_2)_2Ge(C_2H_5)_3$	126 (1.4)		1.4473	1.0935	4-11		128
$(C_2H_5)_3Ge(CH_2)_3Ge(C_2H_5)_3$	128-129 (1.5)		1.4759	1.0807	4-11		128
$(C_2H_5)_3Ge-p-C_6H_4Ge(C_2H_5)_3$	157-158 (2-3)		1.5218		2	90	46
$(C_2H_5)_3Ge-m-C_6H_4Ge(C_2H_5)_3$	149 (1.8)		1.5177		2	64	46
$(C_6H_5)_3GeCH_2CH_2CH_2Ge(C_6H_5)_3$		134-136			4-11	86.5	65
$(C_2H_5)_2Ge \begin{array}{c} \diagup CH_2CH_2 \\ \diagdown \\ \diagup CH_2CH_2 \\ \diagdown \end{array} Ge(n-C_4H_9)_2$	117 (0.6)		1.4932	1.1198	4	17.6	127
D. Tetrasubstituted germanes with functional groups on the side chain							
$(CH_3)_3GeCH_2Cl$	113-114 (761.5)		1.4389 (25)	1.189 (25)	1	79.8	197
$(CH_3)_3GeCH_2I$	154 (752)		1.5112	1.7160	1	24	162
$(CH_3)_3GeCH_2COOH$		43.5			15	48	25
$(CH_3)_3GeCHClCH_3$	127-128 (760)		1.4448	1.1552	1	45	140
$(CH_3)_3GeCH_2CH_2CH_2Cl$	161 (153)		1.4480	1.1172	1	80	136
$(CH_3)_3Ge-p-C_6H_4Br$	118 (20)				1		38
$(CH_3)_3Ge-p-CH_2C_6H_4Cl$	112 (14)		1.5288		1	80	25
$(CH_3)_3Ge-p-C_6H_4COOH$		119.5-121			15		38
$(CH_3)_3Ge-p-CH_2C_6H_4COOH$		173-174			15	40	25
$(C_2H_5)_3GeCH_2CH_2CN$	225-227 (760)				4		115
$(C_2H_5)_3GeCH_2CH_2COOH$	158-160 (10)				4	49	115, 172
$(C_2H_5)_3GeCH_2CH_2CHO$	129-131 (17)				4	60	115
$(C_2H_5)_3GeCH_2COCH_3$	111 (20)		1.4604	1.0763	6		115, 172
$(C_2H_5)_3GeCH_2COC_6H_5$	135 (3)				6	35	115, 172
$(C_2H_5)_3GeCH_2COOC_2H_5$	222-224 (760)				6	37	172
$(C_2H_5)_3GeCH_2CHOHCH_2OH$	128 (0.5)		1.4837	1.1566	11		128
$(C_2H_5)_3GeCH_2CH_2CH_2OOCCH_3$	116.5 (11)		1.4540	1.0704	4	50	136
$(C_2H_5)_3GeCHBrCH_2CH_2COOC_2H_5$	152 (2)		1.4871	1.2082	11		128
$(C_2H_5)_3GeCH_2CH_2SCH_2COOH$	160 (0.8)		1.5060	1.1959	11		128
$(C_2H_5)_3GeCH_2CH_2CH_2OH$	89-90 (3)		1.4695	1.0775	1	73	45
$(C_2H_5)_3GeCH_2CH_2CH_2Cl$	120.5 (128)		1.4680	1.1172	1	82	136
					4	5	136
$(C_2H_5)_3GeCH_2CH(CH_2)CH_2Cl$	107 (12)		1.4710	1.0820	1	51	136
					4	36	136
$(C_2H_5)_3GeCH_2CH_2CH_2SCH_2COOH$	168 (0.8)		1.5005	1.1161	11		128

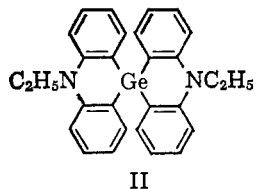
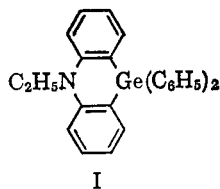
TABLE III (Continued)

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
(C ₂ H ₅) ₂ GeCH ₂ CH ₂ CH ₂ SCH ₂ CH ₂ OH	150 (0.7)		1.5027	1.1158	11		128
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ F	121 (15.5)		1.4998		1	75	47
(C ₂ H ₅) ₂ Ge- <i>m</i> -C ₆ H ₄ Cl	132-133 (8)		1.5289		1	60	47
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ Cl	130 (6)		1.5287		1	60	47
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ Br	134.5 (4-5)		1.5452		2	83	47
					1	46	38, 99
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ I	127-128 (2)		1.5724		2	80	47
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ NO ₂	118-120 (0.3)		1.5410		16	63	46
(C ₂ H ₅) ₂ Ge- <i>m</i> -C ₆ H ₄ NO ₂	122-124 (0.5-0.6)		1.5365		16	51	46
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ COOH		45-46			15		38
(C ₂ H ₅) ₂ Ge- <i>o</i> -C ₆ H ₄ OCH ₃	128.5-129 (7)		1.5203		2	86	47
(C ₂ H ₅) ₂ Ge- <i>m</i> -C ₆ H ₄ OCH ₃	128.5 (6)		1.5205		2	85	47
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ OC ₂ H ₅	131-133 (11-12)		1.5136		3	65	47
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ OC ₆ H ₅	179 (3)		1.5581		2	89	47
(C ₂ H ₅) ₂ Ge- <i>o</i> -C ₆ H ₄ N(CH ₃) ₂	118 (3-4)		1.5210		2	78	47
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ N(CH ₃) ₂	149 (4.5)		1.5438		2	87	47
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ CH(OH)CH ₃	112-114 (5)		1.5170		10	19.6	99
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ OCH ₃	141 (10)		1.5217		1	79	48
(C ₂ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ CH ₂ CH ₂ OH	95-97 (5)		1.5155		10	72.5	99
(<i>n</i> -C ₃ H ₇) ₂ GeCH ₂ CH ₂ CH ₂ OH	175-180 (20)		1.4715	1.0327	4	62	115, 172
(<i>n</i> -C ₃ H ₇) ₂ GeCH ₂ CH ₂ COOCH ₃	150-154 (18)		1.4595		4	34	115, 172
(<i>n</i> -C ₃ H ₇) ₂ GeCH ₂ CH ₂ CN	168-169 (11)		1.4660	0.9947	4	42	172
(<i>n</i> -C ₃ H ₇) ₂ GeCH ₂ CH(CN)CH ₂ CH ₂ CN	205-207 (13)				4		172
(<i>n</i> -C ₃ H ₇) ₂ GeCH ₂ CH(COOCH ₃)- CH ₂ CH ₂ COOCH ₃	192-195 (18)		1.4648	1.077	4		172
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ Br					11		128
(<i>n</i> -C ₄ H ₉) ₂ GeCHBrCH ₂ Br	147 (0.5)		1.5102	1.3619	11		128
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ CN	168-169 (11)		1.4660	0.9947	4	42	115, 172
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ NH ₂					17	60	172
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ OC ₆ H ₅	187-188 (18)		1.4570	0.9500	4	72	172
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ CCl ₃	156 (0.9)		1.4855	1.1474	11		128
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ CH ₂ OH	153-155 (3)		1.4717	0.999	17	60	172
					4	67	172, 115
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ CH ₂ NH ₂	161 (10)		1.4700	0.9816	4	74	172
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ CH ₂ SH	150 (15)		1.4730	0.9788	4	30	172
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ CHO	125-128 (1)		1.4630	1.0314	4	60	115, 172
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ COOC ₂ H ₅	160-165 (10)		1.4590	1.0271	6	40	115, 172
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH(CN)CH ₂ CH ₂ CN	205-207 (13)				4		172
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ COOCH ₃	175-178 (17)		1.4615	1.0059	4	40	172
(<i>n</i> -C ₄ H ₉) ₂ GeCH ₂ CH ₂ COOC ₂ H ₅	122-124 (0.5)		1.4595	1.0028	4	34	115, 172
(<i>n</i> -C ₅ H ₁₁) ₂ GeCH ₂ COOC ₂ H ₅	188 (14)				6	35	172
(<i>n</i> -C ₅ H ₁₁) ₂ GeCH ₂ CH ₂ CN	193-194 (11)				4		115
(<i>i</i> -C ₅ H ₁₁) ₂ GeCH ₂ CH ₂ CH ₂ CN	128 (0.6)		1.4653	0.9635	4	50	172
(C ₆ H ₁₁) ₂ Ge- <i>p</i> -C ₆ H ₄ Cl		135			2	66	47
(C ₆ H ₁₁) ₂ Ge- <i>p</i> -C ₆ H ₄ OCH ₃		132.5			2	84	47, 48
(C ₆ H ₁₁) ₂ Ge- <i>p</i> -C ₆ H ₄ N(CH ₃) ₂		190			2	78	47
C ₇ H ₁₅ Ge(CH ₂ CH ₂ OC ₄ H ₉) ₂	180 (0.4)		1.4570	0.9638	4	70	172
(C ₆ H ₅) ₂ GeCOOH		188-189 dec.			16	83	31
(C ₆ H ₅) ₂ GeCOOCH ₃		107-108					31
(C ₆ H ₅) ₂ GeCH ₂ OH		115-116			9	31.4	61
					17	35	61
(C ₆ H ₅) ₂ GeCH ₂ Cl		116-118			1	76	65
(C ₆ H ₅) ₂ GeCH ₂ CH ₂ CN		126-129			4	83	84
(C ₆ H ₅) ₂ GeCH ₂ CH ₂ COCH ₃		144-146			4	53	84
(C ₆ H ₅) ₂ GeCH ₂ CH ₂ CONH ₂		176-178			4		84
(C ₆ H ₅) ₂ GeCH ₂ CH ₂ COOCH ₃		60.5-62			4	50	84
(C ₆ H ₅) ₂ GeCH ₂ CH ₂ OOCCH ₃		62-62.5			4	54	84
(C ₆ H ₅) ₂ GeC ₄ H ₉ OH		101-103			9	83.4	72
(C ₆ H ₅) ₂ GeC ₅ H ₁₀ OH		51-61			4	41	84
(C ₆ H ₅) ₂ GeC(OH)(C ₆ H ₅) ₂		153-155			9	37	61
					10	71	61
(C ₆ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ Br		159-160			2	55	22
(C ₆ H ₅) ₂ Ge- <i>p</i> -C ₆ H ₄ COOH		201-202			15	13	22
					13	55	22

TABLE III (Concluded)

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
(C ₆ H ₅) ₃ Ge- <i>m</i> -C ₆ H ₄ COOH		168–169			14	10	22
(C ₆ H ₅) ₃ Ge- <i>p</i> -C ₆ H ₄ COCl		143–145					22
(C ₆ H ₅) ₃ Ge- <i>p</i> -C ₆ H ₄ CONH ₂		171–172					22
(C ₆ H ₅) ₃ Ge- <i>m</i> -C ₆ H ₄ CONH ₂		162–163					22
(C ₆ H ₅) ₃ Ge- <i>p</i> -C ₆ H ₄ CH ₂ OH		108.5–110			2	39	22
(C ₆ H ₅) ₃ Ge- <i>m</i> -C ₆ H ₄ N(CH ₃) ₂		92–93			2	71	22
(C ₆ H ₅) ₃ GeCH(C ₆ H ₅)CH ₂ COC ₆ H ₅		119–120			8	26.4	65
(<i>n</i> -C ₃ H ₇) ₂ Ge(CH ₂ CH ₂ CN) ₂	140 (0.4)		1.4802	1.1058	4	31	172
(<i>n</i> -C ₄ H ₉) ₂ Ge(CH ₂ COOC ₂ H ₅) ₂	190 (12)				5		172
(<i>n</i> -C ₄ H ₉) ₂ Ge(CH ₂ CH ₂ COCH ₃) ₂	155–156 (0.4)		1.477	1.0681	4	27	172
(<i>n</i> -C ₄ H ₉) ₂ Ge(CH ₂ CH ₂ COOCH ₃) ₂	153–155 (0.8)		1.4680	1.1080	4	20	172
(C ₆ H ₅) ₂ GeC ₁₂ H ₁₀ N(C ₂ H ₅) ^d		120–121			2	52.4	71
(C ₂ H ₅)NC ₁₂ H ₁₀ GeC ₁₂ H ₁₀ N(C ₂ H ₅) ^d		212–214			2	18.1	71
E. Alkyl derivatives of the higher germanes							
(CH ₃) ₆ Ge ₂	137 (722)	–40	1.4564 (25)		3	74	33

^a C₄H₈Ge, germanocyclopentane. ^b C₆H₁₀Ge, germanocyclohexane. ^c C₄H₈GeC₅H₁₀, germano-5-spiro-4,5-decane. ^d C₂H₅NC₁₂H₁₀Ge-(C₆H₅)₂, 5-ethyl-5,10-dihydro-10,10-diphenylphenazagermine (I). (C₂H₅NC₁₂H₁₀)₂Ge, 5,5'-diethyl-10,10'-spiro-(5,10-dihydrophenazagermine) (II).



C. ORGANOGERMANIUM HALIDES

Preparation

The following preparative methods (1–7) already discussed in section II have been used to partially substitute R groups on germanium halides.

1. Direct synthesis.
2. Grignard reaction.
3. Organolithium synthesis.
4. Addition of a hydride to a double bond.
5. Organomercury synthesis.
6. Diazo addition.
7. Condensation of a germanium hydride with a halide.
8. Germanium diiodide reacts with trifluoromethyl iodide upon heating at 110–130° for 10 days. The products obtained are trifluoromethyltriiodogermane and a trace of bis-(trifluoromethyl)-diiodogermane (40). The similar reaction of methyl iodide with germanium diiodide was known before 1951 (91).
9. Cleavage of tetraalkyl germanes. The classical method involves cleavage using bromine (91). Lesbre and Mazerolles (112) found that iodine cleaves tetraalkylgermanes in the presence of AlI₃. Dibromides and diiodides can be prepared more readily when AlBr₃ or AlI₃ are used as catalysts (174). Gladshstein, Rode, and Soborovskii cleaved tetramethyl- and tetraethylgermane with HF to obtain the monofluoride in 70% yield (74).

10. Reaction of X₂ or HX with an organogermanium oxide. This is the most common method for preparing organogermanium halides. However, since the oxide is generally prepared by the hydrolysis of a halide, this method cannot be considered a primary method for preparation of halides. Its usefulness is mainly in the more efficient separation of halide mixtures or as an intermediate step in the conversion of one halide

the borohydride reduction is THF, for lithium hydride and lithium deuteride, dioxane.

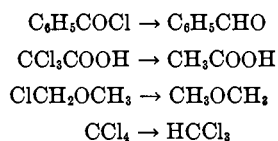
In addition to reduction, organogermanium hydrides have been prepared by two of the general methods discussed in section II.

6. Addition of a hydride to a double bond.
7. Grignard reaction.

Properties

A summary of the reactivity of trialkylgermanium hydrides toward a large variety of organic and inorganic reagents is given by Satge (172). Alkylgermanium hydrides are resistant to solvolysis by basic solution; this behavior differs markedly from the corresponding silanes and stannanes, which undergo solvolysis readily at room temperature (186).

Triethylgermane will reduce inorganic systems with an oxidation potential of –0.6 or less to a lower oxidation state or to the free metal (16). Alkylgermanium hydrides are also rather selective reducing agents for organic systems, carrying out without catalysts such reductions as (173)



Organogermanium hydrides have been used with some success as catalysts in the polymerization of α -monoolefins (202).

TABLE IV
 ORGANOGERMANIUM HYDRIDES

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
CH_2GeH_3	-35.1 (760)	-158			2	50	3, 211
					5		163
$\text{C}_2\text{H}_5\text{GeH}_3$	11.5 (743.5)				1		211
					5	54	163
$n\text{-C}_3\text{H}_7\text{GeH}_3$	30 (760)		1.4130	1.0391	1	85	93
					5	35.3	164
$n\text{-C}_4\text{H}_9\text{GeH}_3$	74 (760)		1.4200	1.0220	2	90	172, 174
$n\text{-C}_5\text{H}_{11}\text{GeH}_3$	104-105 (760)		1.4302	1.0138	2	90	172, 174
$n\text{-C}_6\text{H}_{13}\text{GeH}_3$	128-129 (760)		1.4350	0.9772	2	90	172, 174
$n\text{-C}_7\text{H}_{15}\text{GeH}_3$	85 (74)		1.4390	.9819	2	90	172, 174
$n\text{-C}_8\text{H}_{17}\text{GeH}_3$	80 (31)		1.4422	.9717	2	90	172, 174
$\text{CF}_2\text{CH}_2\text{CH}_2\text{GeH}_3$	46 (750.5)		1.3530	1.3362	5	2.5	164
$(\text{CH}_3)_2\text{GeH}_2$	0.6 (760)	-149			5		163
					2	99	3
					3		216
$(\text{C}_2\text{H}_5)_2\text{GeH}_2$	74 (760)		1.4208	1.0378	2	90	163, 172, 174
$(n\text{-C}_3\text{H}_7)_2\text{GeH}_2$	126-127 (760)		1.4340	1.0030	2	90	172, 174
$(i\text{-C}_3\text{H}_7)_2\text{GeH}_2$	110 (760)		1.432	0.982	2	54	14
$(n\text{-C}_4\text{H}_9)_2\text{GeH}_2$	86 (46)		1.4428	.9782	2	90	172, 174
					4	70	174
$(n\text{-C}_5\text{H}_{11})_2\text{GeH}_2$	92 (12)		1.4478	.9595	2	90	172, 174
$(n\text{-C}_6\text{H}_{13})_2\text{GeH}_2$	113-114 (8)		1.4522	.9484	2	90	172, 174
$(n\text{-C}_7\text{H}_{15})_2\text{GeH}_2$	148 (10)		1.4543	.9348	2	90	172, 174
$(n\text{-C}_8\text{H}_{17})_2\text{GeH}_2$	164-165 (9)		1.4568	.9274	2	90	172, 174
$\text{C}_4\text{H}_9\text{GeH}_2^a$	91-92 (760)		1.4838	1.2261	2	18.6	127
$\text{C}_5\text{H}_{10}\text{GeH}_2^b$	119-120 (760)		1.4835	1.1846	2	20.2	127
$(\text{CH}_3)_3\text{GeH}$	26 (755.5)		1.3890	1.0128	2	90	172
					5		163
$(n\text{-C}_3\text{H}_7)_3\text{GeH}$	183 (742)		1.4340	1.0030	2	90	93, 172
$(i\text{-C}_3\text{H}_7)_3\text{GeH}$	174 (760)		1.4505	0.9770	2	90	172
$(n\text{-C}_4\text{H}_9)_3\text{GeH}$	123 (20)		1.4508	.9490	2	90	115, 172
					4	70	172
$(n\text{-C}_5\text{H}_{11})_3\text{GeH}$	150 (11)		1.4542	.9310	2	90	115, 172
$(i\text{-C}_5\text{H}_{11})_3\text{GeH}$	140 (17)		1.4517	.9238	2	90	115, 172
$(n\text{-C}_6\text{H}_{13})_3\text{GeH}$	122-125 (0.5)		1.4582	.9228	2	90	55, 172
$(n\text{-C}_7\text{H}_{15})_3\text{GeH}$	182 (1.7)		1.4600	.9108	2	90	172
$(n\text{-C}_8\text{H}_{17})_3\text{GeH}$	179-180 (0.4)		1.4610	.9061	2	90	172
$(o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{GeH}$	120-150 (0.001)	119-120			7		75
$(m\text{-CH}_3\text{C}_6\text{H}_4)_3\text{GeH}$	160-170 (0.001)				7		75
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{GeH}$	160 (0.001)	81			7		75
$(1\text{-C}_{10}\text{H}_7)\text{GeH}$		249-250			2	82	215
$(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{GeH}$	62 (755.5)		1.4090	1.0158	5		163
$(n\text{-C}_3\text{H}_7)_2(\text{NCCH}_2\text{CH}_2)\text{GeH}$	75 (0.4)		1.4621	1.0632	6	21	172
$(n\text{-C}_3\text{H}_7)_2(\text{HOOCCH}_2\text{CH}_2)\text{GeH}$	140-142 (0.5)	30			6	30	172
$(n\text{-C}_4\text{H}_9)_2(\text{C}_2\text{H}_5\text{OOCCH}_2)\text{GeH}$	132-134 (12)		1.4540	1.0521	7	28	172
$(n\text{-C}_4\text{H}_9)_2(\text{CH}_3\text{OOCCH}_2\text{CH}_2)\text{GeH}$	121 (12)		1.4621	1.0383	6	30	172
$(n\text{-C}_4\text{H}_9)_2(\text{CH}_3\text{OOCCH}_2\text{CH}_2)\text{GeH}$	112-113 (1)		1.4568	1.0545	6	30	172
$(n\text{-C}_4\text{H}_9)_2(\text{C}_6\text{H}_5)\text{GeH}$	140 (9)				7	20	172
$(n\text{-C}_4\text{H}_9)_2(\text{C}_6\text{H}_5\text{CH}_2)\text{GeH}$	150-160 (15)				7	28	172
$(n\text{-C}_5\text{H}_{11})_2(\text{OCH}_2\text{CH}_2\text{C}(\text{CH}_3)\text{H})\text{GeH}$	139-140 (10)		1.4585	0.9910	6	44	172
$(\text{C}_6\text{H}_5\text{CH}_2)_2(n\text{-C}_7\text{H}_{15})\text{GeH}$	180 (1)		1.514	1.079	7	15	127
$(\text{C}_6\text{H}_{10})(\text{C}_6\text{H}_5)\text{GeH}^b$	128 (14)		1.5550	1.1989	2	82	127

^a $\text{C}_4\text{H}_9\text{Ge}$, germanocyclopentane. ^b $\text{C}_6\text{H}_{10}\text{Ge}$, germanocyclohexane.

to another. The seven general methods listed above usually result in a mixture of chlorides or bromides: R_3GeX , R_2GeX_2 , and RGeX_3 ; such a mixture is difficult to separate by distillation. If the mixture is converted to the oxides, separation by fractional distillation is

generally more efficient; the separated oxides can then be reconverted to the desired halides.

11. Reaction of HX or X_2 with an organogermanium hydride. The reaction of I_2 with $n\text{-C}_4\text{H}_9\text{GeH}_3$ or $(n\text{-C}_4\text{H}_9)_2\text{GeH}_2$ gives complete substitution of iodine

TABLE V
 ORGANOGERMANIUM DEUTERIDES

Compound	B.p. (mm.), °C.	n_D^{20}	d_4^{20}	Yield, %	Reference
CH ₃ GeD ₃	-23.5 (745)			52	163
C ₂ H ₅ GeD ₃	11.3 (748.5)			56	163
C ₄ H ₉ GeD ₃	41.5 (754)	1.4055	1.0508	29	164
CH ₂ =CHCH ₂ GeD ₃	37 (744)	1.4320	1.1146	24	164
(CH ₃) ₂ GeD ₂	6.5 (745)			67	163
(C ₂ H ₅) ₂ GeD ₂	71.5 (743.5)	1.4200	1.0525		163
(CH ₃) ₃ GeD	26 (758)	1.3893	1.0207	70	163
(C ₂ H ₅) ₃ GeD	120 (740)	1.4333	1.0097	31	164
(CH ₃) ₂ (C ₂ H ₅)GeD	60 (737.4)	1.4083	1.0262		163

All these compounds were prepared by the reduction of organogermanium chlorides using lithium deuteride.

for hydrogen if reflux with Cu catalyst is used. At room temperature without catalysis substitution at a single hydrogen takes place (17, 18). Using AlCl₃ as a catalyst, hydrochloric acid at room temperature reacts with (CH₃)₂GeH₂ and (CH₃)GeH₃ to form a mixture of the mono- and disubstituted products (3). At 100° the disubstituted product is formed. Under the same conditions, however, HBr gives mainly monosubstitution (77).

12. Reaction of RX with organogermanium hydrides. Organic halides and acid chlorides react with alkylgermanium hydrides to give alkylgermanium halides in good yield. Reactivity and yield are in the order: I > Br > Cl and RGeH₃ > R₂GeH₂ > R₃GeH. The more reactive cases are exothermic; reactions with mono- and dihydrides require reflux conditions (117, 125, 172). If an excess of dihydride is used, along with a reduced reaction time, substitution at only one of the hydrogens can be obtained (117, 172). In a similar reaction, a mixture of (C₂H₅)₂GeX₂ (X = Br, Cl) and (C₂H₅)₃GeH, upon refluxing 2 hr. with AlCl₃ catalyst, gave (C₂H₅)₂GeHX in about 50% yield (117, 172).

13. Redistribution reactions. Although phenyltrichlorogermane had previously been prepared by the reaction of germanium tetrachloride with tetraphenylgermane, attempts to prepare alkylgermanium halides in this way had been unsuccessful. The use of aluminum halides as catalysts has recently allowed this reaction to be employed successfully. Mazerolles (125) has prepared dibromodiethylgermane, bromotriethylgermane, and dibromodi-*n*-butylgermane by heating germanium tetrabromide with the tetraalkylgermane in the presence of aluminum tribromide. Van der Kerk, Rijkens, and Janssen (212) have studied the reaction between tetra-*n*-butylgermane and germanium tetrachloride in the presence of aluminum chloride in the temperature range 120–200°. The products are mainly tri- and di-*n*-butylgermanium chlorides, the trichloride not being obtained in high yield. Adjustment of mole ratios and reaction temperatures govern the relative proportions of the products. It is presumed that the reaction proceeds by means of an alkylaluminum intermediate.

Aluminum chloride also catalyzes a reaction between tetraalkylgermanes and alkyl halides. Triethylgermanium chloride and bromide have been prepared in this way by refluxing tetraethylgermane with isopropyl halide (166).

14. Side chain chlorination using SO₂Cl. Sulfuryl chloride will chlorinate the alkyl group of alkyltrichlorogermanes preferentially at the β-position in the presence of benzoyl peroxide catalyst. In the chlorination of C₂H₅GeCl₃ the ratio of α to β products is 1:9. This reagent does not chlorinate methyltrichlorogermane. In this respect the Cl₃Ge- group is considerably more β-directing than Cl₃Si- (140, 159).

15. Side chain photochlorination. Photochlorination of methyltrichlorogermane at 150° in an apparatus in which the chlorinated products were removed from the reaction zone gave a mixture of CH₂ClGeCl₃ (18.5%), CHCl₂GeCl₃ (43%), and CCl₃GeCl₃ (trace). In the same way (CH₃)(CH₂Cl)GeCl₂ was prepared from (CH₃)₂GeCl₂. Adjustment of reaction conditions allowed the principal product to be obtained in 51% yield, with lesser amounts of more highly chlorinated products (140, 162).

16. Other chlorinating agents. Several inorganic chlorides will convert organogermanium hydrides into chlorides; generally 6–8 hr. reflux is necessary for this reaction. The halides which have been used for this reaction are GeCl₄, AlCl₃, CCl₄, and SO₂Cl. With triethyl- and tri-*n*-butylgermanium hydrides, yields are in the range 75–90% (172).

17. Halogenation with HgX₂. Mercuric halides give substitution at one hydrogen on *n*-butylgermanium trihydride and di-*n*-butylgermanium dihydride to give compounds of the type RGeH₂X and R₂GeHX in high yield (17).

18. Halogen interconversions. Anderson (11, 18) has used SbF₃ to convert dibromides and diiodides quantitatively to difluorides. In a mixture of di- and tri-*n*-propylgermanium bromides produced from a Grignard reaction, separation was achieved by treatment with SbF₃. The dibromide was converted to the difluoride, while the monobromide reacted only slightly after heating 1 hr.

Ponomarenko and Vzenkova (162) have used the Swarts reaction to convert mono-, di-, and trimethylgermanium chlorides and bromides to fluorides.

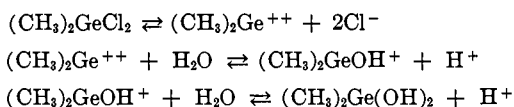
Hydrogen bromide replaces chlorine in R_{4-n}GeCl_n even when the R group includes a double bond. 2-Methyltrichlorogermane is an exception; however, in this compound addition at the double bond does take place (139).

Sodium iodide in acetone solution reacts overnight without heating with tri-*n*-hexylgermanium chloride, precipitating NaCl, and giving the organogermanium iodide in good yield (55).

Properties

Initial work on conducting solutions of organogermanium halides in dimethylformamide had led to the conclusion that ions, such as, R_3Ge^+ , R_2Ge^{++} , and RGe^{+++} were formed (73). More recent work has shown that the conductance is due to reaction of the halides with water in the incompletely purified solvent (211a).

In water solution dissociation is followed by hydrolysis, with the following equilibria



Over the concentration range 0.0760–0.0019 *M* the *i*-factor (number of particles in solution) is approximately five, and the titration curve is that of a strong acid (170). The rates of hydrolysis of triphenylchlorogermane, some of its derivatives, and silicon analogs have been measured by fast reaction techniques. The germanes are hydrolyzed more slowly than the silanes. This has been taken as evidence for the greater π -bond stability of the Si–O bond (39).

In liquid hydrogen chloride, triphenylchlorogermane is only slightly soluble. Attempts to detect the presence of the $(C_6H_5)_3Ge^+$ ion in this system, corresponding to the known $(C_6H_5)_3C^+$ ion, which is present under the same circumstances, were not successful (154).

The dipole moments of several organogermanium halides have been determined by the heterodyne beat method (98, 152). The results are listed in Table VI. From these it has been calculated that the Ge–C bond has 15% double bond character (98).

The trifluoromethylgermanium trihalides hydrolyze in warm water or aqueous NaOH to give fluoroform. When an aqueous solution of trifluoromethyltrifluorogermane is treated with sodium fluoride, potassium trifluoromethylpentafluorogermanate, $K_2CF_3GeF_5$, is formed (40).

Organogermanium halides containing both Ge–H and Ge–X bonds were first prepared by Anderson (17). They are more reactive toward halogens and halides and less reactive toward hydrolysis than their silicon analogs. Hydrolysis of these compounds with aqueous sodium hydroxide results in destruction of the Ge–H

bonds. The vapor pressure curves and Trouton constants of CH_3GeH_2Br , CH_3GeHCl_2 , and $(CH_3)_3GeBr$ have been determined by Griffiths and Onyszchuk (77).

D. ORGANOGERMANIUM HALOGENOIDS

Preparation

1. Action of silver salt on an organogermanium halide. The only organogermanium halogenoids known in 1951 were the three ethylgermanium isocyanates prepared by this reaction, which remains the standard preparative method for germanium isocyanates (5, 7, 12, 14, 18). Silver cyanide has been used to prepare several organogermanium cyanides. Anderson (4, 14) prepared but did not purify or characterize $C_2H_5Ge(CN)_3$, $(i-C_3H_7)_2Ge(CN)_2$, and $(i-C_3H_7)_3GeCN$ by this method. Seyferth and Kahlen (194) have prepared $(CH_3)_3GeCN$ in 61% yield by the action of $AgCN$ on $(CH_3)_3GeI$.

2. Action of an acid on an organogermanium oxide. Hydrogen thiocyanide reacts with di- and trialkylgermanium oxides to form the corresponding thiocyanide in high yield (80%). The reaction is exothermic and complete in 2 hr. Hydrogen cyanide will react with trialkylgermanium oxides only. Hydrogen cyanate does not react in this manner (4).

3. Action of a mercuric salt on a hydride. This reaction is similar to the corresponding reaction of mercuric halides (see section C, preparative method 17). It has been used to prepare $(n-C_4H_9)_2GeHX$ ($X = NCS, CN$). An excess of the hydride, gradual addition of the mercuric salt, and reflux of about 90 min. are necessary (18).

4. Seyferth and Kahlen prepared trimethylgermanium thiocyanate by heating $(CH_3)_3GeCN$ with sulfur for 5 hr. at 175–180° (194).

5. If boron trifluoride dietherate is added to $(CH_3)_3GeCN$ and the ether distilled off, a solid addition compound is formed in 85% yield (194).

6. $(CH_3)_2Ge(CNS)_2$ was prepared by adding $(CH_3)_2GeCl_2$ to a solution containing CNS^- ion followed by evaporation. It was proposed that the reaction consisted of the combination of $(CH_3)_2Ge^{++}$ ions with thiocyanate ions (170).

Chemical Properties

The organogermanium cyanides and thiocyanides are colorless mobile liquids, readily soluble in ethanol, diethyl ether, and petroleum ether (5).

$(CH_3)_3GeCN:BF_3$ is a solid crystalline compound, soluble in ether and acetone, less soluble in benzene. It liquefies in moist air (194).

Anderson (14) has prepared a conversion series for organogermanium halides, halogenoids, and esters. Upon treatment with the silver salt and refluxing, re-

TABLE VI

DIPOLE MOMENTS OF ORGANOGERMANIUM HALIDES

Compound	Dipole moment, D.	Reference
CH_3GeCl_3	2.63	98
$(CH_3)_2GeCl_2$	3.11	98
$C_2H_5GeCl_3$	2.87	98
	2.28	152
$(C_2H_5)_2GeCl_2$	3.19	98
$(CH_3)_3GeCHClCH_3$	2.34	98
$Cl_3GeCH_2CH_2Cl$	2.41	98

TABLE VII
 ORGANOGERMANIUM HALIDES

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
A. Trihalides							
CH ₃ GeF ₃	96.5 (751)	38			18		162
CH ₃ GeBr ₃	168 (750)		1.5770	2.6337	1	20.2	162
C ₂ H ₅ GeCl ₃	141.5 (761)		1.4745	1.6091	4	55	158, 162
<i>n</i> -C ₃ H ₇ GeCl ₃	167 (767)		1.4779	1.5146	1		152
					1		171
					2		171
					3	16	93
					4	85	45, 164
<i>i</i> -C ₃ H ₇ GeCl ₃	164.5 (767)		1.4760		1		171
<i>n</i> -C ₄ H ₉ GeCl ₃	184 (760)		1.4750	1.4520	1	26.9	17
					4	75	45
					13	25	212
<i>i</i> -C ₄ H ₉ GeCl ₃	108 (25)		1.4732	1.4465	4		136
<i>n</i> -C ₄ H ₉ GeBr ₃	237 (760)		1.5548	2.1480	10	67	17
					18	96	139
<i>n</i> -C ₄ H ₉ GeI ₃	119-121 (1)			2.647	11	92	17
<i>n</i> -C ₅ H ₁₁ GeCl ₃	101-103 (40)				4	21	168
<i>n</i> -C ₆ H ₁₃ GeCl ₃	97 (14)		1.4719 (25)	1.565	4	22	53, 168
					12	96	172
<i>n</i> -C ₇ H ₁₅ GeCl ₃	101-103 (10)				4	18	168
<i>n</i> -C ₈ H ₁₇ GeCl ₃	150 (15)		1.4720	1.2712	4	55	158, 168
<i>i</i> -C ₈ H ₁₇ GeCl ₃	78-82 (0.6)				4	10	168
<i>n</i> -C ₁₀ H ₂₁ GeCl ₃	87-90 (0.1)				4	9	168
C ₆ H ₁₁ GeCl ₃	79 (3)		1.5130	1.4792	4		136
C ₆ H ₅ CH ₂ GeCl ₃	111-118 (18)	35-37			7		136
C ₆ H ₅ CH ₂ CH ₂ GeCl ₃	132 (10)		1.5550	1.4816	4	30	45
C ₅ H ₇ GeCl ₃	87 (11)		1.5270	1.5327	4	58	45, 141
C ₅ H ₉ GeCl ₃	84.3-84.5 (12)		1.5070	1.5210	4	75	141
ClCH ₂ GeCl ₃	149 (759)		1.5003	1.8415	6	94	197
					15	19	140, 162
CHCl ₂ GeCl ₃	168-179 (760)		1.5100	1.8166	15	13	140
					4		45
CCl ₃ GeCl ₃	130 (200)	106-107			15		162
CF ₃ GeF ₃		3			18		40
CF ₃ GeCl ₃					18		40
CF ₃ GeI ₃	40-42 (0.001)				8		40
CH ₃ CHClGeCl ₃	167 (746.5)		1.4948	1.6975	14	4	140, 159
ClCH ₂ CH ₂ GeCl ₃	188 (746.5)		1.5094	1.7587	4	52	158, 138
					14	32	159, 140
CF ₂ HCH ₂ GeCl ₃	140 (752)		1.4490	1.7992	4	47	164
ClCH ₂ CHClGeCl ₃	88 (12)		1.5240	1.8390	4	62	138
CHCl ₂ CH ₂ GeCl ₃	74 (10)		1.5176	1.8166	4	62	45
(C ₂ H ₂ Cl ₃)GeCl ₃	92 (9)		1.5341	1.9000	4	55.3	138
Cl ₂ CHCCl ₂ GeCl ₃	123 (25)		1.5378	1.9243	4	48	138
CH ₂ ClCH(CH ₂)GeCl ₃	68-69 (7)		1.5036	1.6442	4		136
CH ₃ CHClCH ₂ GeCl ₃	98 (32)		1.5007	1.6418	4		136
CF ₃ CH ₂ CH ₂ GeCl ₃	143 (758)		1.4233	1.7105	4	29	164
ClCH ₂ CH ₂ CH ₂ GeCl ₃	105 (20)		1.5070	1.6636	4	77.4	136, 158
NCCH ₂ CH ₂ GeCl ₃	135 (22)	37.7			4	53	158
<i>i</i> -ClC ₄ H ₉ GeCl ₃	92 (11)		1.5000	1.5758	4	58.3	158
CH ₃ CHClCH ₂ CH ₂ CH ₂ GeCl ₃	79-82 (0.4)				4	10	168
(CH ₃) ₂ CBrCH ₂ GeBr ₃	123-128 (8)		1.5920	2.3822	18	62	139
CH ₃ COOCH ₂ CH ₂ GeCl ₃	127.5 (12)		1.4855	1.5923	4	57	45, 158
C ₆ H ₁₂ ClGeCl ₃	89-91 (0.2)				4	16	168
C ₆ H ₁₁ F ₂ GeCl ₃	75-76 (2)				4	22	168
<i>p</i> -ClC ₆ H ₄ GeCl ₃	105-107 (5)		1.5738	1.6467	7	16	203a
ClFCHCF ₂ OCH ₂ CH ₂ CH ₂ GeCl ₃	120-123 (10)		1.4523	1.6817	4	44	164
B. Dihalides							
(CH ₃) ₂ GeF ₂	112 (750)		1.3743	1.5726	18		162
(CH ₃) ₂ GeBr ₂	153 (746)		1.5268	2.1163	1		162
					2	25	162

TABLE VII (Continued)

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
(C ₂ H ₅) ₂ GeBr ₂	82 (12)		1.5272	1.8811	18	89	139
					13	85	126
(<i>n</i> -C ₃ H ₇) ₂ GeF ₂	182.8 (764)	0.5	1.4128	1.248	10		9
(<i>n</i> -C ₃ H ₇) ₂ GeCl ₂	209.5 (760)	-45	1.4725	1.275	10	100	9
					3	20	93
(<i>n</i> -C ₃ H ₇) ₂ GeBr ₂	240.5 (760)	-52	1.5173	1.689	10	100	9
(<i>n</i> -C ₃ H ₇) ₂ GeI ₂	276.5 (760)	-53.5		2.024	10	96	9
(<i>i</i> -C ₃ H ₇) ₂ GeF ₂	174 (760)	-24	1.4146	1.222	18		11
(<i>i</i> -C ₃ H ₇) ₂ GeCl ₂	203 (760)	-52	1.4738	1.268	10	100	11
(<i>i</i> -C ₃ H ₇) ₂ GeBr ₂	234 (760)	-22	1.519	1.670	10	100	11
(<i>i</i> -C ₃ H ₇) ₂ GeI ₂	268 (760)	-9	1.597	2.008	10	100	11
(<i>n</i> -C ₄ H ₉) ₂ GeF ₂	216 (760)	10	1.4222	1.183	18	99	18
(<i>n</i> -C ₄ H ₉) ₂ GeCl ₂	242 (760)		1.4724	1.208	10	98	18
					12	100	172
					13	80	212
(<i>n</i> -C ₄ H ₉) ₂ GeBr ₂	269 (760)		1.5109	1.565	12	95	117, 172
					11	99	18
					13	73	126
(<i>n</i> -C ₄ H ₉) ₂ GeI ₂	304 (760)		1.5770	1.863	12	95	117, 172
					11	99	18
(C ₆ H ₅) ₂ GeI ₂		68-69			5	69	52
(<i>o</i> -C ₆ H ₄) ₂ GeI ₂		85-86.5			5	45.7	52
C ₄ H ₈ GeCl ₂ ^a	94 (64)		1.5101	1.5239	18	67	127
C ₄ H ₈ GeBr ₂ ^a	97 (15)		1.5720	2.0806	12	76	127
C ₄ H ₈ GeI ₂ ^a	107 (5)		1.6770	2.5000	12	74	127
C ₅ H ₁₀ GeCl ₂ ^b	99 (24)		1.5107	1.4675	18	91	127
					10	87	127
C ₅ H ₁₀ GeBr ₂ ^b	115 (17)		1.5659	1.9775	12	91	127
C ₅ H ₁₀ GeI ₂ ^b	108 (2)		1.6610	2.3698	10	82	127
					12	76.6	127
(ClCH ₂)(CH ₃)GeCl ₂	155 (760)		1.4930	1.6694	6	78	197
					14	51	162
(ClCH ₂) ₂ GeCl ₂	90 (21)		1.5176 (25)		6		197
(CF ₃) ₂ GeI ₂					8		40
(<i>o</i> -ClC ₆ H ₄) ₂ GeI ₂		124-125.5			5	58.3	52
(<i>m</i> -ClC ₆ H ₄) ₂ GeI ₂		61-63			5	73	52
(<i>p</i> -ClC ₆ H ₄) ₂ GeI ₂		67.5-69			5	74	52
(<i>o</i> -BrC ₆ H ₄) ₂ GeI ₂		155.5-157.5			5	68	52
(<i>o</i> -C ₂ H ₅ OC ₆ H ₄) ₂ GeI ₂		137-138			5	50	52
CH ₃ GeHCl ₂	113.2 (760)	-63.1			11	33	3, 77
C. Monohalides							
(CH ₃) ₃ GeF	76 (746)		1.3863	1.2300	18		162
					9	71	74
(CH ₃) ₃ GeCl	102 (760)	-14	1.4283 (29)	1.2382 (21.5)	2	15	180
					3	30-35	180, 162
					9		77
(CH ₃) ₃ GeBr	113-114 (760)		1.4713	1.5486	2	22	162
					9		172
(C ₂ H ₅) ₃ GeF	147-148 (744)		1.4206	1.5127	9	71	74
(C ₂ H ₅) ₃ GeCl	179.5 (760)		1.4650	1.175	10		16
					12	100	172
					16	87	172
					13	60	166
(C ₂ H ₅) ₃ GeBr	190.9 (760)		1.4862	1.4009	10		16
					18	80	139
					12	86.6	166
					13	70	126, 166
(C ₂ H ₅) ₂ GeI	213.3 (760)		1.528	1.608	10		16
(<i>n</i> -C ₃ H ₇) ₃ GeF	203 (760)	-27.5	1.4340	1.074	10	100	5
(<i>n</i> -C ₃ H ₇) ₂ GeCl	227 (760)	-70	1.4641	1.100	10	100	5
(<i>n</i> -C ₃ H ₇) ₃ GeBr	242 (760)	-47	1.4832	1.282	10	93	5
(<i>n</i> -C ₃ H ₇) ₂ GeI	259 (760)	-38	1.5144	1.433	10	85	5

TABLE VII (Concluded)

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
(<i>i</i> -C ₃ H ₇) ₃ GeF	198 (760)	-65	1.433	1.069	10		11
(<i>i</i> -C ₃ H ₇) ₃ GeCl	222 (760)		1.472	1.100	10		11
(<i>i</i> -C ₃ H ₇) ₃ GeBr	234 (760)	-45	1.4852	1.231	2		11
(<i>i</i> -C ₃ H ₇) ₃ GeI	254 (760)	4	1.524	1.446	10		11
(<i>n</i> -C ₄ H ₉) ₃ GeF	245 (760)	-12	1.4419	1.038	11	80	7
(<i>n</i> -C ₄ H ₉) ₃ GeCl	271 (760)		1.4652	1.054	2	60	221
					10	100	7
					16	90	172
					12	80	117, 172
					13	80	212
(<i>n</i> -C ₄ H ₉) ₃ GeBr	279 (760)		1.4809	1.195	10	100	7
					12	95	172
(<i>n</i> -C ₄ H ₉) ₃ GeI	297 (760)		1.5002	1.340	10		7, 69
					12	95	172
(<i>i</i> -C ₄ H ₉) ₃ GeI	137-138 (13)		1.5098	1.3543	9		112
(<i>n</i> -C ₄ H ₁₁) ₃ GeI	184-185 (11)		1.5023	1.2686	9		112
(<i>i</i> -C ₆ H ₁₁) ₃ GeI	177-178 (13)		1.5002	1.254	12		117
(<i>n</i> -C ₆ H ₁₃) ₃ GeCl	138-139 (0.5)		1.4661	0.989	10	74	55
(<i>n</i> -C ₆ H ₁₃) ₃ GeBr	143-145 (0.5)		1.4763 (27)	1.117 (26)	2	40	55
(<i>n</i> -C ₆ H ₁₃) ₃ GeI	154-155 (0.5)		1.4935 (26)	1.188 (26)	18	56	55
(C ₆ H ₅) ₃ GeI		155-157			5	37	52
(<i>o</i> -CH ₃ C ₆ H ₄) ₃ GeBr	195 (0.01)	119-120			5		75
(<i>m</i> -CH ₃ C ₆ H ₄) ₃ GeI		76-77.5			5	60	52
(<i>p</i> -CH ₃ C ₆ H ₄) ₃ GeCl		128-129			2		75
(<i>p</i> -CH ₃ C ₆ H ₄) ₃ GeBr		121			2		75
(1-C ₁₀ H ₇) ₃ GeBr		242-243.5			2	38	215
(2-C ₁₀ H ₇) ₃ GeI		174-176			5	23.5	52
(CH ₃) ₂ (C ₂ H ₅)GeCl	125 (760)				2		163
(CH ₃) ₂ (C ₂ H ₅)GeBr	143 (775)		1.4726	1.4952	2		163
(<i>n</i> -C ₄ H ₉)(C ₂ H ₅) ₂ GeBr	100 (12)		1.4828	1.3075	10		127
(C ₄ H ₉)(C ₆ H ₅)GeBr ^a	116 (0.9)		1.5878	1.5438	8	90	127
(C ₆ H ₁₀)(C ₆ H ₅)GeBr ^b	125 (0.8)		1.5828	1.5045	8	93	127
(ClCH ₂) ₂ (CH ₃)GeCl	95-97 (30)		1.5010 (25)		6	79.8	197
(<i>p</i> -ClC ₆ H ₄) ₃ GeI		133-134.5			5	7	52
(<i>p</i> -BrC ₆ H ₄) ₃ GeI		170-171			5	41.6	52
(<i>p</i> -CH ₃ OC ₆ H ₄) ₃ GeI		114-115			5	61.6	52
(<i>p</i> -C ₂ H ₅ OC ₆ H ₄) ₃ GeI		95.5-97			5	62	52
CH ₃ GeH ₂ Cl	70.9 (760)	-101			10	34	3
CH ₃ GeH ₂ Br	80.5 (760)	-89.2			11	53	77
(CH ₃) ₂ GeHCl	89.4 (760)	-76			10	17	3
(C ₂ H ₅) ₂ GeHCl	136 (760)		1.4572	1.2409	12	80	117, 172
(C ₂ H ₅) ₂ GeHBr	153 (760)		1.4888	1.5340	12	80	117, 172
(C ₂ H ₅) ₂ GeHI	70 (23)		1.5382	1.7717	12	40	117, 172
<i>n</i> -C ₄ H ₉ GeH ₂ Cl	140 (760)		1.4598	1.246	17	82	17
<i>n</i> -C ₄ H ₉ GeH ₂ Br	159 (760)		1.4910	1.536	17	78	17
<i>n</i> -C ₄ H ₉ GeH ₂ I	181 (760)		1.5412	1.776	11	70	17
(<i>n</i> -C ₄ H ₉) ₂ GeHCl	219 (760)		1.4618	1.107	17	97	17
					12	80	172
(<i>n</i> -C ₄ H ₉) ₂ GeHBr	234 (760)		1.4832	1.305	17	92	17
(<i>n</i> -C ₄ H ₉) ₂ GeHI	249 (760)		1.5148	1.470	11	57	17
C ₄ H ₉ GeHI ^a	107 (48)		1.5956	1.9924	11	80	127
C ₆ H ₁₀ GeHI ^b	132 (58)		1.5835	1.8681	11	73	127
D. Miscellaneous							
Cl ₃ GeCH ₂ CH ₂ GeCl ₃	130 (12)	56			4	90	158
Cl ₃ GeCH ₂ CH ₂ CH ₂ GeCl ₃	123 (5)	25.5	1.5314 (25)	1.6538	4		45, 136
Cl ₃ GeCH ₂ CH(CH ₃)CH ₂ GeCl ₃	156 (20)		1.5290	1.8010	4	56.5	136
Cl ₃ GeCH(CH ₂ Cl)CH ₂ GeCl ₃	140-143 (7)		1.5520	1.9394	4 + 7	57	136
(<i>n</i> -C ₄ H ₉) ₂ IGe-GeI(<i>n</i> -C ₄ H ₉) ₂					5		90
Br(C ₆ H ₅) ₂ GeGe(C ₆ H ₅) ₂ Br		167-169			3	60	133
Br ₂ (C ₆ H ₅)GeGe(C ₆ H ₅)Br ₂		113-117			3	20	133

^a (C₄H₉)Ge, germanocyclopentane. ^b (C₆H₁₀)Ge, germanocyclohexane.

TABLE VIII
 ORGANOGermanium HALOGENOIDS

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	Reference
$(\text{CH}_3)_2\text{Ge}(\text{NCS})_2$	266–268 (760)	45.5–47			6		170
$(\text{C}_2\text{H}_5)_2\text{Ge}(\text{NCS})_2$	298 (760)	16		1.356	2	80	4
$(i\text{-C}_3\text{H}_7)_2\text{Ge}(\text{NCO})_2$	239 (760)		1.464	1.225	1	100	14
$(i\text{-C}_3\text{H}_7)_2\text{Ge}(\text{NCS})_2$	296 (760)		1.558	1.234	2	80	14
$(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{NCS})_2$	337 (760)		1.5501	1.201	2	76	18
$(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{NCO})_2$	273 (760)		1.4634	1.179	1	67	18
$(\text{CH}_3)_3\text{GeCN}$		38–38.5			1	70.5	194
$(\text{CH}_3)_3\text{GeSCN}$	191.5–193 (760)		1.4960 (22)		4	90.5	194
$(\text{CH}_3)_3\text{GeCN}:\text{BF}_3$		85–87			5	85	194
$(\text{C}_2\text{H}_5)_3\text{GeCN}$	213 (760)	18	1.4509	1.111	2		4
$(\text{C}_2\text{H}_5)_3\text{GeNCS}$	252 (760)	–46	1.517	1.184	2	80	4
$(n\text{-C}_3\text{H}_7)_3\text{GeNCS}$	287 (760)	–56	1.5063	1.105	2	80	4
$(n\text{-C}_3\text{H}_7)_3\text{GeCN}$	253 (760)	–13	1.4544	1.041	2		4
$(n\text{-C}_3\text{H}_7)_3\text{GeNCO}$	247 (760)	–19	1.4575	1.055	1		5
$(i\text{-C}_3\text{H}_7)_3\text{GeNCS}$	277 (760)	18	1.512	1.112	2		11
$(i\text{-C}_3\text{H}_7)_3\text{GeNCO}$	238 (760)		1.4602	1.097	1	96	12
$(n\text{-C}_4\text{H}_9)_3\text{GeNCS}$	319 (760)		1.5039	1.071	2	80	4
$(n\text{-C}_4\text{H}_9)_3\text{GeNCO}$	283 (760)	–47	1.4595	1.044	1	100	7
$(n\text{-C}_4\text{H}_9)_2\text{GeH}(\text{NCS})$	96–98 (1)		1.5097	1.123	3	77	18
$(n\text{-C}_4\text{H}_9)_2\text{GeH}(\text{CN})$	108–110 (8)		1.4527	1.050	3	72	18

placement will take place according to the order $\text{I} \rightarrow \text{S} \rightarrow \text{Br} \rightarrow \text{CN} \rightarrow \text{NCS}, \text{Cl} \rightarrow \text{NCO} \rightarrow \text{O}, \text{OCOR} \rightarrow \text{F}$.

It has been shown that the organosilicon cyanides consist of an equilibrium mixture of the cyano and isocyno forms. A comparison of the infrared spectra of trimethylcyanogermane and its boron trifluoride addition compound with the spectra of the analogous silicon compounds indicates that they are also a mixture of isomeric forms (194).

E. ORGANOGermanium OXIDES AND HYDROXIDES

Preparation

1. Hydrolysis. The basic hydrolysis of organogermanium halides continues to be the main preparative method for organogermanium oxides. Generally such hydrolysis results in formation of the oxide; however, with the triisopropylgermanium (11) and tri-1-naphthylgermanium (215) halides, basic hydrolysis results in the germanol, probably due to steric factors.

2. Reaction of silver carbonate with a halide. Triisopropylgermanium oxide, which does not result from basic hydrolysis of the halide, has been prepared by the action of silver carbonate on the iodide (11). Trimethylgermanium oxide, which had been previously prepared by hydrolysis, but not isolated, has been prepared in pure form by this method (77). Attempts to prepare an oxide with the formula $(\text{CH}_3\text{GeH}_2)_2\text{O}$ by reaction of silver carbonate with $\text{CH}_3\text{GeH}_2\text{Br}$ were not successful; instead, complex methylgermoxane-polymers were obtained (77).

The following two general reactions, discussed in section II, have been used to prepare oxides directly.

3. Diazo addition.

4. Diarylmercury synthesis.

5. Heat. Organogermanium hydroxides are converted to the oxides on heating, with loss of water. In the only case studied since 1951, that of tri-1-naphthylgermanol, this conversion is very slow, the reaction not being complete after heating at 170° for 24 hr. (215).

In the two cases where the different polymeric forms of R_2GeO have been extensively studied, the trimeric form is obtained by heating. Trimeric diphenylgermanium oxide can be obtained from either the tetrameric or the polymeric form by vacuum distillation (134). Similarly, trimeric dimethylgermanium oxide can be obtained by heating either of the other two forms of this oxide under vacuum at $210\text{--}220^\circ$ (35).

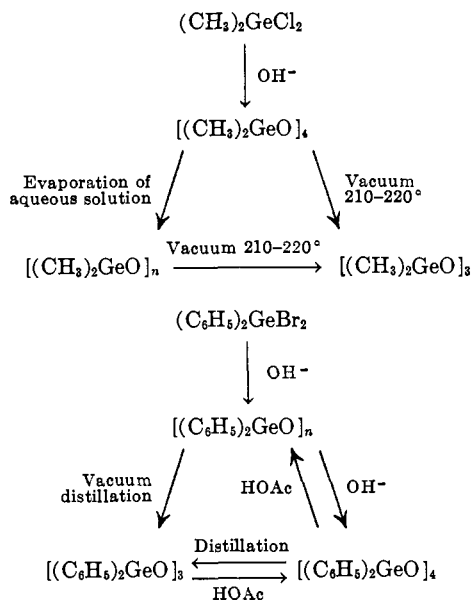
6. Reaction with oxygen. Germanocyclopentane, upon agitation in an atmosphere of oxygen, forms a trimeric oxide $[\text{C}_4\text{H}_8\text{GeO}]_3$. Germanocyclohexane, under similar conditions, gives a mixture of a tetrameric oxide and $\text{C}_6\text{H}_{10}\text{GeH}(\text{OH})$, the first compound prepared with both Ge–H and Ge–O bonds (127).

Properties

Several organogermanium oxides of the type R_2GeO exist in isomeric forms. The two which have been most extensively studied since 1951 have been the dimethyl (35) and diphenyl (134) oxides. The interrelations of the forms of these oxides are indicated in the diagrams on the next page.

The amorphous form $[(\text{CH}_3)_2\text{GeO}]_n$ is insoluble in benzene, cyclohexane, and carbon tetrachloride, soluble in ethanol, acetic acid, and water. The water solution contains monomeric units (35).

Hydrolysis of the reaction mixture of a diarylmercury (see section II-D) reaction gave three separate



products corresponding to the formula $(p\text{-ClC}_6\text{H}_4)_2\text{GeO}$: an ether-soluble fraction; a benzene-soluble fraction, whose molecular weight as found corresponded to a tetramer; and an insoluble, infusible fraction. All three were obtained in very small yield (52).

Refluxing tri-1-naphthylgermanol for 3 hr. with formic acid gives a white solid, insoluble in organic solvents, which does not melt or decompose up to 300° . This substance is probably a mixture of polymeric 1-naphthylgermanium oxides (215).

Cryoscopic measurements of the water solution of trimethylgermanium oxide indicate that it is present in solution as the germanol. Attempts to isolate pure $(\text{CH}_3)_3\text{GeOH}$, however, have not been successful (24).

The relative tendency of the Group IV triphenyl hydroxides to act as Lewis acids and bases in hydrogen bonding has been used to measure the extent of dative bonding between the metal ion and the oxygen. Such bonding decreases markedly from silicon to germanium to tin (217). The reaction rates of $(\text{C}_6\text{H}_5)_3\text{MOH}$ (M represents C, Si, Ge) with *N,N*-diethylaminotrimethylsilane have been studied by Pike (160). The rates were in the order $\text{Si} > \text{Ge}, \text{C}$.

F. ALKOXYGERMANES

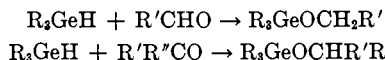
Preparation

1. Synthesis using sodium alkoxide. This method was used for the synthesis of the only two members of this series prepared previous to 1951, the tetraethoxy and tetraphenoxy compounds (91). It has been replaced as the most common preparative method by method 2. Alkylchloro-germanes react with sodium alkoxides to give mixed alkyl-alkoxygermanes (30, 77, 218). An attempt to prepare $(\text{CH}_3)_2\text{GeH}_2\text{OCH}_3$ by the addition of NaOCH_3 to $\text{CH}_3\text{GeH}_2\text{Br}$ was unsuccessful,

the products being methanol and a polymeric material (77).

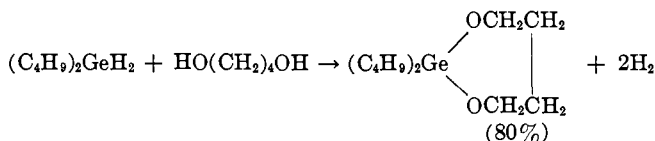
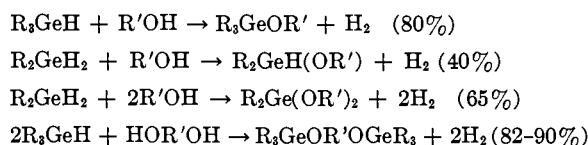
2. Direct synthesis using ammonia or pyridine. Bradley, Kay, and Wardlaw (27) prepared tetraalkoxygermanes by passing ammonia vapor into a solution of germanium tetrachloride and alcohol in benzene. An exothermic reaction takes place, at first in the vapor phase, then in solution, with precipitation of NH_4Cl (27, 132). Abel (1) has shown that this reaction proceeds in the presence of pyridine, although at a slower rate. Pike and Fournier (161) have prepared mono-, di-, and trialkoxychloro-germanes by varying the ratio of alcohol to tetrachloride in the pyridine-catalyzed reaction.

3. Addition of a hydride to a carbonyl group. Lesbre and Satge (118) have shown that trialkylgermanium hydrides react with aldehydes and ketones in the presence of copper powder to give alkoxides in good yield.



Reflux times of 24–48 hr. are required. The reaction between tri-*n*-butylgermanium hydride and cyclohexanone does not require a catalyst.

4. Reaction of a hydride with a hydroxyl group. Lesbre and Satge (119) have also prepared organo-germanium alkoxides by heating alkylgermanium hydrides with organic hydroxy compounds in the presence of copper powder. This reaction has been found to take place with primary and secondary alcohols, glycols, phenol, and hydroquinone.



5. Phenol reacts with germanium tetrachloride to give tetraphenoxygermane upon long refluxing in benzene (150 hr.). The yield and product purity are better than those obtained in the synthesis using ammonia (132).

6. Alcohol interchange. Higher members of this series can be prepared from lower members by refluxing a mixture of alcohol and alkoxide, followed by distillation of the lower boiling alcohol (27). Mehrotra and Chandra (132) have prepared a series of ethoxyphenoxy compounds by reacting stoichiometric ratios of phenol with tetraethoxygermane. The mixed alkoxygermanes so prepared, however, decompose upon distillation into mixtures of ethoxy- and phenoxygermanes.

TABLE IX
 ORGANOGermanium OXIDES AND HYDROXIDES

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	Reference
(<i>n</i> -C ₃ H ₇ GeO) ₂ O		285–290 dec.			1		93
(<i>n</i> -C ₄ H ₉ GeO) ₂ O					1	93	17
(C ₆ H ₅ GeO) ₂ O					3	27.3	144
<i>m</i> -CH ₃ C ₆ H ₄ GeOOH					4	0.5	52
(<i>p</i> -ClC ₆ H ₄ GeO) ₂ O					4	1.6	52
(<i>p</i> -BrC ₆ H ₄ GeO) ₂ O					3	1.2	144
(<i>p</i> -CH ₃ OC ₆ H ₄ GeO) ₂ O					3		144
(<i>p</i> -C ₂ H ₅ OC ₆ H ₄ GeO) ₂ O					3		144
[(CH ₃) ₂ GeO] ₃					5		35
[(CH ₃) ₂ GeO] ₄		91–92			1	67	35
[(CH ₃) ₂ GeO] _{<i>n</i>}		132–133			1		35
[(<i>n</i> -C ₃ H ₇) ₂ GeO] ₃	320 (760)	5.8	1.4730	1.240	1		9
[(<i>n</i> -C ₄ H ₉) ₂ GeO] ₄					1		93
[(<i>i</i> -C ₃ H ₇) ₂ GeO] ₃	321 (760)	44			1	100	11
[(<i>n</i> -C ₄ H ₉) ₂ GeO] ₃	180–182 (1)	–17	1.4712	1.161	1	94	18
[(C ₆ H ₅) ₂ GeO] ₃	300 (2)	149			1		134
					5		134
[(C ₆ H ₅) ₂ GeO] ₄		218			1		134
[(C ₆ H ₅) ₂ GeO] _{<i>n</i>}		298			1		134
(<i>p</i> -CH ₃ C ₆ H ₄) ₂ GeO		221.5–222.5			4	79	52
[(<i>m</i> -CH ₃ C ₆ H ₄) ₂ GeO] ₃		83–84			4	26.9	52
(C ₄ H ₉ GeO) ₃ ^a		166			1	79	127
					6		127
(C ₆ H ₁₀ GeO) ₄ ^b		144			1		127
					6		127
(<i>p</i> -ClC ₆ H ₄) ₂ GeO		257–262			4	40.4	52
[(<i>p</i> -ClC ₆ H ₄) ₂ GeO] ₄		243–247			1		52
[(<i>m</i> -ClC ₆ H ₄) ₂ GeO] ₄		158–159			4	24.9	52
(<i>p</i> -BrC ₆ H ₄) ₂ GeO					4	80	52
(<i>p</i> -CH ₃ OC ₆ H ₄) ₂ GeO		281–301			4	9.4	52
[(<i>p</i> -C ₂ H ₅ OC ₆ H ₄) ₂ GeO] ₂		130–136			4	6.9	52
(2-C ₁₀ H ₇) ₂ GeO		211–212			4	4.8	52
[(CH ₃) ₂ Ge] ₂ O	129 (760)	–61.1	1.4712		2	61	77
[(<i>n</i> -C ₃ H ₇) ₂ Ge] ₂ O	305 (760)	–55	1.4148	1.068	1	66	5
[(<i>i</i> -C ₃ H ₇) ₂ Ge] ₂ O	119–120 (1)		1.4836	1.112	2	87	11
(<i>i</i> -C ₃ H ₇) ₃ GeOH	216 (760)	–15	1.472	1.077	1	100	11
[(<i>n</i> -C ₄ H ₉) ₂ Ge] ₂ O	353 (760)	–42	1.4652	1.027	1		7
[(C ₆ H ₁₃) ₂ Ge] ₂ O	210–211 (0.04)		1.4645 (25)	0.963 (25)	1	57	55
[(1-C ₁₀ H ₇) ₂ Ge] ₂ O		206–208			5		215
(1-C ₁₀ H ₇) ₃ GeOH		130–140 dec.			1	95	215
C ₆ H ₁₀ GeHOH ^b	130–131 (9)		1.5085		6		127

^a Germanocyclopentane. ^b Germanocyclohexane.

7. Trimethylmethoxygermane and boron trifluoride give a solid addition compound upon standing overnight at room temperature (77).

Properties

The germanium tetraalkoxides are readily hydrolyzed in moist air to polymeric germanium oxides. Tetraisopropoxygermane gives a mixed alkoxygermanium oxide [(*i*-C₃H₇O)₃Ge]₂O in addition to the polymer (187).

Hydrogen chloride reacts exothermically with (C₆H₅O)₄Ge to give phenol and GeCl₄ (132).

A variety of reagents cleave the Ge–O bond in alkoxygermanes, adding at the germanium atom. Thus benzoyl chloride, benzene sulfonic acid, hydrogen iodide, lithium aluminium hydride, formic acid, acetic acid, and acetic anhydride all cleave compounds of the type R₃GeOR. The Ge–O bond in alkoxy compounds is thus more readily cleaved than in organogermanium oxides which are stable to acetic acid and cleaved only with difficulty by formic acid (118).

The densities, surface tensions (27), vapor pressures, and viscosities (28) of the tetraalkoxygermanes have been measured.

TABLE X
 GERMANIUM ALKOXIDES

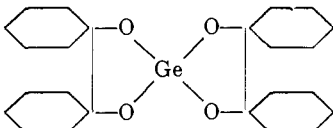
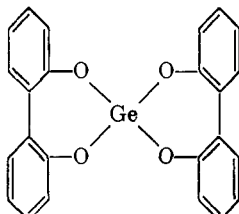
Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
$(\text{CH}_3\text{O})_4\text{Ge}$	145.5 (760)	23.5	1.3968 (25)	1.3244 (25)	1 2	21	92, 187 27
$(\text{C}_2\text{H}_5\text{O})_4\text{Ge}$	185.5 (760)	-72	1.4061	1.1288 (25)	1 2	65 73	92 1, 27
$(n\text{-C}_3\text{H}_7\text{O})_4\text{Ge}$	238-239 (722)		1.4168	1.0565 (25)	1 2 6	57 79	92 1 27
$(i\text{-C}_3\text{H}_7\text{O})_4\text{Ge}$	81.5 (0.7)			1.0245 (25)	1 6		27 27, 187
$(n\text{-C}_4\text{H}_9\text{O})_4\text{Ge}$	299 (760)		1.4271	1.0167 (25)	1 2 6	74 91	92 1, 27 27
$(i\text{-C}_4\text{H}_9\text{O})_4\text{Ge}$	264.5 (760)			1.0054 (25)	1 6		27 27
$(s\text{-C}_4\text{H}_9\text{O})_4\text{Ge}$	257 (760)			1.0164 (25)	1 6		27 27
$(t\text{-C}_4\text{H}_9\text{O})_4\text{Ge}$	224 (760)	44		1.0574 (25)	1 2		209 27
$(n\text{-C}_5\text{H}_{11}\text{O})_4\text{Ge}$	120-123 (0.03)		1.4335 (25)	0.9941 (25)	1 2 6	55	92 27 27
$[\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2\text{O}]_4\text{Ge}$				1.0425 (25)	2		27
$(n\text{-C}_6\text{H}_{13}\text{O})_4\text{Ge}$	150-153 (0.04)		1.4372 (25)	0.9682 (25)	1	56	92
$(\text{C}_6\text{H}_{11}\text{O})_4\text{Ge}$	166-167 (0.01)	ca. -65			1	21	92
$(\text{C}_6\text{H}_5\text{O})_4\text{Ge}$	210 (0.1)				2 5 6	31 77 65	132 132 132
$(\text{CH}_2\text{FCH}_2\text{O})_4\text{Ge}$	157-158 (0.15)				2	54.4	143
$(\text{CCl}_3\text{CH}_2\text{O})_4\text{Ge}$	187 (0.03)				2	20.4	143
$(\text{C}_2\text{H}_5\text{O})_2\text{Ge}(\text{OC}_6\text{H}_5)$	80-83 (9) dec.				6	100	132
$(\text{C}_2\text{H}_5\text{O})_2\text{Ge}(\text{OC}_6\text{H}_5)_2$					6	100	132
$(\text{C}_2\text{H}_5\text{O})\text{Ge}(\text{OC}_6\text{H}_5)_3$	222 (0.3) dec.				6	100	132
		279			2	86	143
		330			6	90.7	143
$\text{CH}_3\text{Ge}(\text{OCH}_3)_3$	136.5-138 (760)		1.4053 (25)	1.264 (25)	1	66	218
$(\text{C}_2\text{H}_5\text{O})_3\text{GeCl}$	181.5-183 (760)				2	12	161
$(i\text{-C}_3\text{H}_7\text{O})_3\text{GeCl}$	58-60 (1.2)		1.4135 (27)		2	46	161
$(t\text{-C}_4\text{H}_9\text{O})_3\text{GeCl}$	72.5-74 (0.8)		1.4227 (25)		2	24	161
$(\text{CH}_3)_2\text{Ge}(\text{OCH}_3)_2$	118-118.5 (763)		1.4093 (25)	1.207 (25)	1	77	218
$(\text{C}_2\text{H}_5\text{O})_2\text{GeCl}_2$	160-164 (760)				2	11	161
$(i\text{-C}_3\text{H}_7\text{O})_2\text{GeCl}_2$	59-61 (8.2)		1.4228 (27)		2		161
$(t\text{-C}_4\text{H}_9\text{O})_2\text{GeCl}_2$	59-60 (0.5)		1.4313 (25)		2		161
$(n\text{-C}_4\text{H}_9\text{O})_2\text{GeCl}_2$	83-86 (4.8)				6	24	161
$(n\text{-C}_6\text{H}_{13}\text{O})_2\text{GeCl}_2$	120-125 (760)		1.4414 (28)		6	26	161
$(\text{C}_6\text{H}_{11}\text{O})_2\text{Ge}(n\text{-C}_4\text{H}_9)_2$	149 (0.5)		1.4473	1.0468	4	80	119
$(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{OCH}_2\text{CH}_3)_2$	135 (10)		1.4648	1.1025	4	80	119

TABLE X (Concluded)

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
(CH ₃) ₃ GeOCH ₃	91.1 (760)	-102.2	1.401 (25)	1.075 (25)	1	98	71, 218
(CH ₃) ₃ GeOCH ₃ :BF ₃	25 sublm.	41-46			7		77
(C ₂ H ₅) ₃ Ge- <i>n</i> -OC ₂ H ₇	190 (760)		1.4388	1.0250	4	100	119
(C ₂ H ₅) ₃ Ge- <i>n</i> -OC ₄ H ₉	209 (755)		1.4406	1.0250	4	100	119
(C ₂ H ₅) ₃ GeOC ₇ H ₁₅	127 (10)		1.4460	0.9852	3	100	118
(C ₂ H ₅) ₃ GeOC ₈ H ₁₇	134 (18)		1.4695	1.0612	3	100	118
(C ₂ H ₅) ₃ GeOC ₆ H ₁₃	140 (18)		1.5102	1.1329	4	90	119
(C ₂ H ₅) ₃ GeOCH ₂ C ₆ H ₅	150-152 (18)		1.5030	1.1103	3	80	118
(<i>n</i> -C ₄ H ₉) ₃ GeOCH(C ₂ H ₅)C ₄ H ₉	160 (9)		1.4532	0.9504	3	50	118
(<i>n</i> -C ₄ H ₉) ₃ GeOCH(CH ₃)C ₆ H ₁₃	180 (12)		1.4540	0.9452	3	50	118
(<i>n</i> -C ₄ H ₉) ₃ GeOC ₆ H ₁₁	180 (16)		1.4680	0.9963	3	60	118
					4	80	119
(C ₆ H ₅) ₃ GeOCH ₃		59-62			1	97	30
C ₂ H ₅ OGeCl ₃	40 (36)				2	27	161
<i>i</i> -C ₃ H ₇ OGeCl ₃	154-160 (760)				2	55	161
<i>t</i> -C ₄ H ₉ OGeCl ₃	37-39 (4.5)				2	20	161
(C ₂ H ₅) ₃ GeO(CH ₂) ₂ OGe(C ₂ H ₅) ₃	162 (11)		1.4640	1.1490	4	82	119
(C ₂ H ₅) ₃ GeO(CH ₂) ₄ OGe(C ₂ H ₅) ₃	151 (1)		1.4650	1.1191	4	90	119
(C ₂ H ₅) ₃ GeO- <i>p</i> -C ₆ H ₄ OGe(C ₂ H ₅) ₃	157 (0.35)		1.5103	1.1931	4	88	119

G. ORGANOGermanium PEROXIDES

Preparation

Davies and Hall (42) first prepared organogermanium peroxides by the reaction of hydrogen peroxide or organic hydroperoxides with germanium chlorides in the presence of tertiary amines. The reaction occurs upon gentle reflux in pentane solution for 1/2 hr. The amine hydrochloride is filtered off, leaving the peroxide. The reactions between germanium tetrachloride and 1-methyl-1-phenylethyl hydroperoxide, 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide, and *t*-butyl hydroperoxide did not result in the expected product. Similarly *t*-butyl hydroperoxide and peroxyoctanoic acid did not give the expected monoperoxy compounds with tri-*n*-propylgermanium chloride (42).

Rieche and Dahlmann (169) have prepared phenylgermanium peroxides, Ph₃GeOOR and [Ph₃Ge]₂OO, by converting triphenylgermanium bromide to the amine and reacting it with organic hydroperoxides or hydrogen peroxide.

Properties

The germanium peroxides are stable at room temperature but decompose when heated above 70°. All hydrolyze readily giving germanium oxide and the original peroxide (42). Hydrochloric acid regenerates the germanium chloride and the peroxide (169). The germanium peroxides catalyze vinyl polymerization and oxidize iodide ion quantitatively (42).

H. ORGANOGermanium ESTERS OF ORGANIC ACIDS

Preparation

1. Reaction of an organic acid with an organogermanium oxide. This method is discussed in Johnson's

TABLE XI

ORGANOGermanium PEROXIDES

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	Reference
(1-C ₁₀ H ₁₇ OO) ₂ Ge		84-85		42
(<i>n</i> -C ₈ H ₁₇) ₂ Ge(OO-1-C ₁₀ H ₁₇) ₂	95 (0.01)			42
<u>CH₂CH₂CH₂CH₂CH₂Ge-</u>				
[OO(C(CH ₃) ₂) ₂]	65 (0.2)	-35	1.4553	42
(CH ₃) ₃ GeOO-1-C ₁₀ H ₁₇	65 (0.5)			42
(<i>n</i> -C ₈ H ₁₇) ₂ GeOOC(CH ₃) ₂	35 (0.001)		1.4383	42
(<i>n</i> -C ₈ H ₁₇) ₂ GeOO-1-C ₁₀ H ₁₇	70 (0.01)	ca. 20	1.4779	42
(C ₆ H ₅) ₃ GeOOC(CH ₃) ₂		55-57		169
(C ₆ H ₅) ₃ GeOOC(CH ₃) ₂ C ₆ H ₅		104-106		169
(C ₆ H ₅) ₃ GeOOC(C ₆ H ₅) ₂		188-195		169
(<i>n</i> -C ₈ H ₁₇) ₂ GeOOGe(<i>n</i> -C ₈ H ₁₇) ₂	65 (0.1-0.05)		1.4608	42
(C ₆ H ₅) ₂ GeOOGe(C ₆ H ₅) ₂		146-148		169

review (91) and has continued in general use since 1951. It fails, however, for the di- and triisopropylgermanium esters (11).

2. Action of silver salts of acids on organogermanium halides. This reaction is essentially the same reaction as the corresponding reaction of silver halogenoids (see section D, preparative method 1). For tri-*n*-butylgermanium esters, this method of preparation is more rapid and gives a higher yield than the preparation from the oxide (method 1) (7). Silver benzoate and silver monochloroacetate do not react with ethyltrichlorogermane (10). In the preparation of ethylgermanium triformate, lead formate was used in place of the silver salt (10).

The silver salt of triphenylgermane carboxylic acid reacts with triphenylbromogermane upon 2-hr. reflux in benzene solution to give triphenylgermyltriphenylgermane carboxylate, (C₆H₅)₃GeCOOGe(C₆H₅)₃, in 51% yield. The sodium salt gives the same product in 81% yield (31).

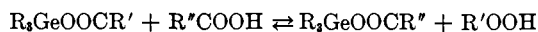
3. Reaction of an acid with an organogermanium hydride. Tri-*n*-butylgermane reacts with acetic acid in the presence of copper powder to give tri-*n*-butyl-

TABLE XII
 GERMANIUM ESTERS OF ORGANIC ACIDS

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	Reference
$C_2H_5Ge(OOCH)_3$	118 (9)	13	1.452	1.617	2		10
$C_2H_5Ge(OOCC_2H_5)_3$	249 (760)	49	1.444	1.393	2	95	10
$C_2H_5Ge(OOCC_2H_5)_2$	256 (760)		1.4434	1.271	2	95	10
$C_2H_5Ge(OOC-n-C_3H_7)_3$	136-137 (2)		1.4432	1.186	2	95	10
$C_2H_5Ge(OOC-n-C_4H_9)_3$	305 (760)		1.4456	1.136	2	95	10
$(CH_3)_2Ge(OOCC_2H_5)_2$	188 (760)	50			1		10
$(n-C_3H_7)_2Ge(OOCC_2H_5)_2$	244.6 (760)	35.6			1	90	9
$(n-C_3H_7)_2Ge(OOCC_2H_4Cl)_2$	143-145 (2)		1.4793	1.374	4		9
$(i-C_3H_7)_2Ge(OOCC_2H_5)_2$	236 (760)		1.445	1.193	2	80	14
					4	80	14
$(i-C_3H_7)_2Ge(OOCC_2H_4Cl)_2$	298 (760)		1.480	1.372	4	98	14
$(i-C_3H_7)_2Ge(OOCC_2H_4CH_3)_2$	255 (760)		1.447	1.146	2	80	14
$(i-C_3H_7)_2Ge(OOCC_2H_4CH_2Cl)_2$	140-142 (1)		1.474	1.294	4		14
$(i-C_3H_7)_2Ge(OOC-n-C_3H_7)_2$	274 (760)		1.452	1.112	2	80	14
					4	78	14
$(i-C_3H_7)_2Ge(OOCC_2H_5)_2$	385 (760)	54			2	80	14
$(C_2H_5)_2GeOOCCH_2Cl$	234 (760)		1.4672	1.243	1	100	13
$(C_2H_5)_2GeOOCCH_2Br$	244 (760)		1.4842	1.423	1		13
$(C_2H_5)_2GeOOCCH_2I$	254 (760)		1.5112	1.593	1		13
$(C_2H_5)_2GeOOCCHCl_2$	248 (760)		1.4672	1.304	1		13
$(C_2H_5)_2GeOOC_2F_5$	183 (760)		1.402	1.272	3	95	16
$(C_2H_5)_2GeOOC_2Cl_4$	125-126 (3)		1.4790	1.368	1		13
$(C_2H_5)_2GeOOC_2C_2H_5$	119-120 (50)		1.4486	1.109	1		13
$(C_2H_5)_2GeOOCCH_2CN$	98-99 (1)		1.464	1.194	4	90	13
$(C_2H_5)_2GeOOCCH_2CH_2Cl$	236 (760)		1.4672	1.210	2	92	13
$(C_2H_5)_2GeOOCCHClCH_3$	235 (760)		1.4619	1.201	2	100	13
$(C_2H_5)_2GeOOCCH_2CH_2Br$	85-86 (1)		1.4832	1.376	4	90	13
$(C_2H_5)_2GeOOCCHBrCH_3$	74-75 (1)		1.4725	1.370	4	90	13
$(C_2H_5)_2GeOOCCH_2CH_2I$	94-96 (1)		1.5002	1.544	4	95	13
$(C_2H_5)_2GeOOC_2F_6$	189.6 (760)		1.3844	1.324	3	99	16
$(C_2H_5)_2GeOOC_3H_7$	221 (760)		1.4486	1.084	1		13
$(C_2H_5)_2GeOOC_3F_7$	201 (760)		1.3780	1.383	3	97	16
$(C_2H_5)_2GeOOC-n-C_4H_9$	230 (760)		1.4467	1.062	2	90	13
$(C_2H_5)_2GeOOC_6H_5$	290 (760)		1.513	1.172	2	90	15
$(C_2H_5)_2GeOOC_6H_4NH_2$	331 (760)		1.544	1.215	4	90	15
$(n-C_3H_7)_2GeOOCH$	233 (760)		1.4505	1.094	1		6
$(n-C_3H_7)_2GeOOCCH_3$	236 (760)		1.4464	1.071	1	98	6
$(n-C_3H_7)_2GeOOCCH_2Cl$	143 (10)		1.4640	1.166	1		6
$(n-C_3H_7)_2GeOOCCH_2Br$	149 (10)		1.4778	1.325	1		6
$(n-C_3H_7)_2GeOOCCHCl_2$	150 (10)		1.4708	1.226	1		6
$(n-C_3H_7)_2GeOOC_2F_5$	226 (760)		1.4103	1.189	1		6
$(n-C_3H_7)_2GeOOC_2H_5$	246 (760)		1.4473	1.054	1	100	6
					4	80	14
$(i-C_3H_7)_2GeOOCCH_3$	229 (760)		1.4532	1.070	2	90	12
$(i-C_3H_7)_2GeOOCCH_2Cl$	269 (760)		1.4722	1.182	2		12
$(i-C_3H_7)_2GeOOCCH_2Br$	98-99 (1)		1.4872	1.331	1	100	12
$(i-C_3H_7)_2GeOOCCH_2I$	281 (760)		1.5090	1.465	1	100	12
$(i-C_3H_7)_2GeOOCCHCl_2$	275 (760)		1.4772	1.236	1	100	12
$(i-C_3H_7)_2GeOOC_2F_5$	220 (760)		1.4200	1.178	1	96	12
$(i-C_3H_7)_2GeOOC_2Cl_4$	107-109 (1)		1.4850	1.291	1	100	12
$(i-C_3H_7)_2GeOOC_2C_2H_5$	242 (760)		1.4538	1.059	2	100	12
$(i-C_3H_7)_2GeOOCCH_2CH_2Cl$	97-99 (1)		1.4717	1.154	2	89	12
$(i-C_3H_7)_2GeOOCCHClCH_3$	269 (760)		1.4672	1.144	2	81	12
$(i-C_3H_7)_2GeOOC-n-C_3H_7$	256 (760)		1.4532	1.045	2	100	12
$(i-C_3H_7)_2GeOOC-n-C_4H_9$	266 (760)		1.4560	1.034	2	93	12
$(i-C_3H_7)_2GeOOC_6H_5$	317 (760)		1.5138	1.132	2		12
$(n-C_4H_9)_2GeOOCH$	267 (760)		1.4538	1.051	1		7
$(n-C_4H_9)_2GeOOC_2F_5$	262 (760)		1.419	1.144	1	100	7
$(n-C_4H_9)_2GeOOC-n-C_6H_{13}$	147-148 (1)		1.4539	0.988	4		7
$(n-C_4H_9)_2GeOOCCH_3$	272 (760)		1.4514	1.027	2		7
$(C_6H_5)_2GeOOC(C_6H_5)_2$		163-164			1	84	30
					2	81	31
					5	86	31

germanium acetate in 60% yield (119). Triethylgermanium hydride reacts with organic haloacids and with the mercury salt of acetic acid, upon refluxing 1-3 hr., to give triethylgermanium esters in good yield (16).

4. Transesterification. Upon heating a mixture of an organogermanium ester and an organic acid, an equilibrium is set up



The more volatile acid can be distilled off, leaving the ester of the other acid in quantitative yield (6). This reaction does not seem to be dependent on the relative dissociation constants of the acids (9).

5. Triphenylgermane carboxylic acid upon being heated at about 200° for 5 min. undergoes a thermal rearrangement with evolution of carbon monoxide and water; $(\text{C}_6\text{H}_5)_3\text{GeCOOGe}(\text{C}_6\text{H}_5)_3$ is obtained in 86% yield (31).

Properties

All of the organogermanium esters are colorless liquids, soluble in a variety of organic solvents. They do not hydrolyze readily in water because of insolubility but do so rapidly in alcoholic NaOH (6).

The organogermanium haloesters tend to decompose at the boiling point giving products with hydrolyzable halogen (6, 9). The order of stability is $\text{F} > \text{Cl} > \text{Br} > \text{I}$. The more halogen atoms in the acid and the closer they are to the germanium atom, the greater the tendency to decompose (13). Thus the attempted preparation of $(n\text{-C}_3\text{H}_7)_3\text{GeOCCCl}_3$ both by methods 1 and 4 was not successful (6).

Triphenylgermyltriphenylgermane carboxylate decomposes on heating to 250°, evolving carbon monoxide and water, leaving hexaphenyldigermoxane; similarly, methyltriphenylgermane carboxylate decomposes at 250° to give triphenylmethoxygermane (30).

I. ORGANOGERMANIUM-SULFUR COMPOUNDS

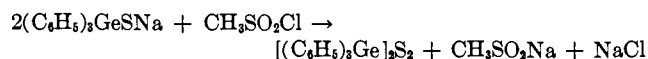
Preparation

1. Action of an inorganic sulfide on a halide. Earlier workers had prepared organogermanium sulfides by the action of hydrogen sulfide or sodium sulfide on an organogermanium halide (91). Since 1951, the only sulfide prepared by this method has been diisopropylgermanium sulfide, which results from the reaction of silver sulfide with diisopropyldiiodogermane. After 30 min. reflux a precipitate of AgI is formed and the sulfide can be obtained by distillation (14).

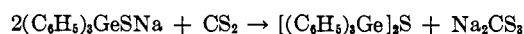
2. Addition of an aqueous solution containing sulfide ion to an acidified aqueous solution of diphenylgermanium oxide trimer results in a precipitate of diphenylgermanium sulfide (167).

3. Reactions of sodium germanethiols. Sodium triphenylgermanethiol reacts with organic halides to form mercaptides; the reaction proceeds readily in

benzene solution at room temperature. The reaction with methane sulfonyl chloride results in hexaphenyldigermanium disulfide rather than the expected thio-sulfonyl compound (83).



The reaction with carbon disulfide results in triphenylgermanium sulfide (83)



4. Reactions of mercaptans with organogermanium esters. This is a typical transesterification reaction. Upon reaction of a mercaptan with the organogermanium ester of a more volatile acid, an equilibrium is set up, and the more volatile acid can be removed by distillation. Anderson (15) has obtained nine triethylgermanium mercaptides by this method from triethylgermanium acetate. In two of these reactions rearrangement occurred. In the reactions by which $(\text{C}_2\text{H}_5)_3\text{Ge-}m\text{-SC}_6\text{H}_4\text{CH}_3$ and $(\text{C}_2\text{H}_5)_3\text{Ge-}o\text{-SC}_6\text{H}_4\text{NH}_2$ were prepared, compounds in which exchange of oxygen for sulfur took place, were also obtained. $(\text{C}_2\text{H}_5)_3\text{Ge-2-SC}_{10}\text{H}_7$ was prepared by the reaction of 2-naphthalenethiol with $(\text{C}_2\text{H}_5)_3\text{GeSC}_6\text{H}_5$ (15).

5. Triethylgermane reacts with butylmercaptan in the presence of platinum catalyst after 72-hr. reflux to form $(\text{C}_2\text{H}_5)_3\text{GeSC}_4\text{H}_9$ in 75% yield. This reaction is analogous to the condensation reaction of organogermanium hydrides with alcohols (see section F, preparative method 4), and is likely to prove to be generally applicable to the preparation of other organogermanium mercaptides (119).

6. Action of sulfuric acid on organic esters. This is also a transesterification reaction, the more volatile organic acid being removed by distillation. Four sulfates have been prepared by Anderson in this manner (6, 9, 14, 15).

7. Benzenesulfonic acid reacts with triethylgermanium hydride upon 6-hr. reflux in toluene solution to give $(\text{C}_2\text{H}_5)_3\text{GeSO}_3\text{C}_6\text{H}_5$ in 70% yield (172).

8. Sodium triphenylgermanethiol is prepared by the addition of triphenylgermanium bromide to a solution of sodium sulfide in ethanol (83).

Properties

All compounds listed in Table XIII are colorless mobile liquids or white crystalline solids, except $(\text{C}_2\text{H}_5)_3\text{GeSC}_6\text{H}_4\text{NH}_2$ and $(\text{C}_2\text{H}_5)_3\text{GeSCH}_2\text{OC}_4\text{H}_9$ which are light yellow liquids (15).

Dimethylgermanium sulfide has been shown to be a trimer, both in the vapor phase and in benzene solution (35).

The mercaptides react slowly with higher boiling mercaptans, with weak organic acids, and with $(\text{C}_6\text{H}_5)_2\text{-SiCl}_2$ (15).

TABLE XIII
 GERMANIUM SULFUR COMPOUNDS

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	Reference
$[(i-C_3H_7)_2GeS]_2$	312 (760)		1.551	1.327	1		14
$[(C_6H_5)_3Ge]_2S$		138.5			2	67	83
$(C_2H_5)_3Ge-n-SC_4H_9$	120 (14)		1.4880	1.0546	5	75	119
$(C_2H_5)_3Ge-n-SC_6H_{13}$	277 (760)		1.488	1.029	3	90	15
$(C_2H_5)_3Ge-n-SC_7H_{15}$	288 (760)		1.489	1.019	3	90	15
$(C_2H_5)_3Ge-n-SC_{12}H_{25}$	357 (760)		1.481	0.975	3	90	15
$(C_2H_5)_3GeSC_6H_5$	286 (760)		1.553	1.153	4	67	15
$(C_2H_5)_3Ge-o-SC_6H_4CH_3$	298 (760)		1.553	1.141	3	90	15
$(C_2H_5)_3Ge-m-SC_6H_4CH_3$	300 (760)		1.550	1.131	3	90	15
$(C_2H_5)_3Ge-o-SC_6H_4NH_2$	326 (760)		1.583	1.197	3	90	15
$(C_2H_5)_3GeSCH_2C_6H_5$	305 (760)		1.549	1.139	3	90	15
$(C_2H_5)_3Ge-2-SC_{10}H_7$	367 (760)		1.613	1.184	3		15
$(C_2H_5)_3GeSCH_2OC_4H_9$	130-132 (1)		1.523	1.177	3	90	15
$(C_2H_5)_3GeSNa$					8		83
$(C_6H_5)_3GeSCH_3$		87-88			2	62	83
$(C_6H_5)_3Ge-n-SC_4H_9$	147-150 (0.5)		1.6135		2	70	83
$(C_6H_5)_3GeSCH_2C_6H_5$		98.5			2	59	83
$(C_6H_5)_3GeSCOC_6H_5$		145.5			2	67	83
$(C_6H_5)_3GeSCH_2SCH_3$		63.0			2	65	83
$(C_6H_5)_3GeSGe(C_6H_5)_2SGe(C_6H_5)_3$		162			2	52	83
$[(C_6H_5)_3Ge]_2S_2$		171-172			2	50	83
$(C_6H_5)_3GeSO_3C_6H_5$	160 (1.3)	38			7	70	172
$[(n-C_3H_7)_2GeSO_4]_2$		129			6		9
$[(i-C_3H_7)_2GeSO_4]_2$		115 dec.			6		14
$[(n-C_3H_7)_3Ge]_2SO_4$	370 (760)			1.186	6		6
$[(i-C_3H_7)_3Ge]_2SO_4$	380 (760)		1.482	1.217	6		12

The sulfates are readily hydrolyzable, benzene-soluble compounds (9, 12).

Sodium triphenylgermanethiol is very hygroscopic, but is stable in dry air; it is soluble in benzene, alcohol, and water and decomposes in alkaline solution to give off H_2S . Upon refluxing in alcohol the sulfide $[(C_6H_5)_3Ge]_2S$ is formed (83).

J. ORGANOGERMANIUM-NITROGEN COMPOUNDS

Previous to 1951 organogermanium nitrogen compounds of the types R_3GeNH_2 , $[R_3Ge]_2NH$, $[R_3Ge]_3N$, R_2GeNH , and $RGeN$ had been prepared. Since 1951 no new compounds of these types have been studied. However, several dialkyl amines, one diazo compound, and an organogermanium nitrate have been described.

Preparation

1. Preparation of germanium dialkyl amines. Dimethyl- and diethyl-amine react with $GeBr_4$ or organogermanium halides at room temperature or below to give the expected germanium amine in good yield. Anderson (8, 18) has prepared five compounds of this type from $GeBr_4$, $C_2H_5GeCl_3$, and $(n-C_4H_9)_2GeCl_2$. Germanium tetrachloride and ethyltrichlorogermane do not give definite organogermanium products upon reaction with aniline (8).

2. Lithium triphenylgermanide reacts with azobenzene or azoxybenzene in THF or GDME at room

temperature to give $(C_6H_5)_3GeN(C_6H_5)NH(C_6H_5)$ in approximately 50% yield (58).

3. The dipyridine-germanium tetrachloride complex reacts with diethylamine upon heating at 120° for 30 hr. to give tetrakis-(diethylamino)-germane in 69% yield (1).

4. Trimethylgermanium nitrate has been prepared by the reaction of silver nitrate with trimethylchlorogermane in THF at room temperature (182).

Properties

The germanium dialkyl amines are colorless mobile liquids, with odors resembling amines. They etch glass easily and have inflammable vapors. The reaction with benzoyl chloride, dichloroacetic acids, or hydrogen iodide is vigorous, resulting in the organogermanium halide (8).

K. ALIPHATIC ORGANOGERMANIUM COMPOUNDS

Petrov, Mironov, and Golgy (159) first reported the preparation of unsaturated organogermanium compounds in 1956. A recent article has reviewed the preparation and reactions, particularly polymerization, of the Group IV unsaturated compounds (157). Two recent reviews of the vinyl derivatives of the metals have appeared (151, 189). Of the methods of preparation listed below, the first seven have already been discussed in section II.

TABLE XIV
 ORGANOGermanium NITROGEN COMPOUNDS

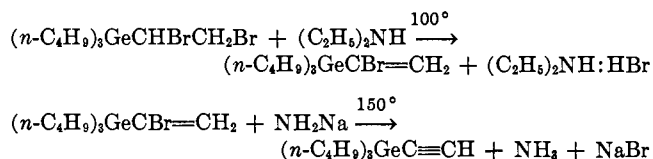
Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	Reference
$[(CH_3)_2N]_4Ge$	203 (760)	14		1.069 (22)	1	80	8
$[(C_2H_5)_2N]_4Ge$	108-110 (2)		1.4726	1.215 (22)	1	45	8
					3	69	1
$(C_2H_5)_3Ge[N(CH_3)_2]_3$	191 (760)	-46		1.049 (22)	1		8
$(C_2H_5)_3Ge[N(C_2H_5)_2]_3$	249 (760)			1.108 (22)	1	90	8
$(n-C_4H_9)_2Ge[N(CH_3)_2]_2$	249 (760)		1.4605	1.001	1	79	18
$(C_6H_5)_3GeN(C_6H_5)NH(C_6H_5)$		142-143			2	58	58
$(CH_3)_3GeONO_2$					4		182

- The Grignard reaction.
 - Reaction of a Grignard reagent with an unsaturated halide.
 - Use of the Grignard reagent of an unsaturated compound.
- Organolithium synthesis.
- Wurtz synthesis.
- Addition of organogermanium hydrides to aliphatic compounds.
- Direct synthesis.
- Divinylmercury synthesis.
- Condensation of a germanium hydride with an organic halide.
- Dehydrohalogenation.

Petrov, Mironov, and Golgy (159) prepared vinyltrichlorogermane by the dehydrochlorination of $CH_2ClCH_2GeCl_3$ using quinoline, after an attempt to prepare this compound by direct synthesis had failed. This reaction required distillation at 200° and gave a rather low yield. This method has been superseded by the use of the vinyl Grignard reagent.

Dehydrochlorination of 1,2-dichloroethyltrichlorogermane using aluminum trichloride gave α -chlorovinyltrichlorogermane in 42% yield; with quinoline the β compound was obtained in 80% yield (138).

Mazerolles (124) has prepared $(n-C_4H_9)_3GeC\equiv CH$ by the dehydrobromination of $(n-C_4H_9)_3GeCHBrCH_2Br$. This reaction was accomplished in two steps



9. Dehydration. Phosphorus oxychloride has been used to dehydrate compounds with hydroxyl groups adjacent to a double or triple bond. Thus $(C_4H_9)_3GeCH=CHC(CH_3)=CH_2$ and $(C_2H_5)_3GeC\equiv CC(CH_3)=CH_2$ are obtained from $(C_4H_9)_3GeCH=CHC(OH)(CH_3)_2$ and $(C_2H_5)_3GeC\equiv CC(OH)(CH_3)_2$, respectively (116, 124).

10. Grignard reactions on the side chain. Kolesnikov and Davydova (99) have prepared $(C_2H_5)_3Ge-p-$

$C_6H_4CH=CH_2$ by reacting the Grignard reagent, $(C_2H_5)_3Ge-p-C_6H_4MgBr$, with vinyl bromide in the presence of cobalt chloride. The yield is rather low and the use of the styryl Grignard reagent (see section II-A) is preferable. Mazerolles (125) has prepared a number of compounds containing triple bonds by the reaction of $R_3GeC\equiv CMgBr$ with organic halides, aldehydes, ketones, and carbon dioxide.

11. Preparation of organogermanium esters of unsaturated acids. Organogermanium esters of unsaturated acids can be prepared by the same methods which have been used in the preparation of similar esters of saturated acids (see section H). Thus triethylgermanium methacrylate has been prepared by the action of methacrylic acid on triethylgermanium chloride (101); triphenylgermanium methacrylate by the reaction between silver methacrylate and triphenylgermanium bromide (53a); and triethylgermanium acrylate by the condensation of acrylic acid with triethylgermane in the presence of copper powder (119).

12. Reaction of hydrogen bromide with unsaturated chlorogermanes. Hydrogen bromide, instead of adding to the double bond in vinyl- and allyltrichlorogermane, gives the tribromogermanium compound. The reaction takes place at room temperature, and no addition occurs even on heating, use of a catalyst, or with excess hydrogen bromide. With methallyltrichlorogermane, both addition and substitution take place (139).

13. Reduction. Vinylgermane has been prepared by Brinckman and Stone (29) through the lithium aluminum hydride reduction of vinyltrichlorogermane. Allylgermane and allyltrideuteriogermane have been prepared by the lithium hydride (or lithium deuteride) reduction of allyltrichlorogermane (164).

14. $(CH_3)_2Ge[C\equiv CCOH(CH_3)_2]_2$ upon heating with acetic anhydride at 80° for 10 hr. gives $(CH_3)_2Ge[C\equiv CC(CH_3)_2OOCCH_3]_2$ in 57% yield (204).

15. $(C_2H_5)_3GeC\equiv CCH_2OH$ and $(C_2H_5)_3GeC\equiv CCHOHC_3H_7$ add to the double bond in $CH_2=CHOC_4H_9$ to give $(C_2H_5)_3GeC\equiv CCH_2OCH(CH_3)OC_4H_9$ and $(C_2H_5)_3GeC\equiv CCH(C_3H_7)OCH(CH_3)OC_4H_9$ (203).

16. Hexavinylidgermane is split by I_2 and Br_2 to give trivinylbromo- and trivinyliodogermane (188).

TABLE XV
 UNSATURATED ORGANOGERMANIUM COMPOUNDS

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
$(\text{CH}_2=\text{CH})_4\text{Ge}$	52-54 (27)		1.4676 (25)	1.040 (25)	1b	35.4	188
$(\text{C}_6\text{H}_5\text{CH}=\text{CH})_4\text{Ge}$		198-200			3	17.5	24
$(\text{CH}_2=\text{CHCH}_2)_4\text{Ge}$	106-107 (15)		1.5030	1.0094	1b		106, 128
$(\text{C}_6\text{H}_5\text{C}\equiv\text{C})_4\text{Ge}$		187-188			2	60	24
$(\text{CH}_2=\text{CH})_3\text{GeBr}$	58 (10)		1.5057 (25)		16	23	188
$(\text{CH}_2=\text{CH})_3\text{GeI}$	71-74 (12)				16	45.6	188
$(\text{CH}_2=\text{CH})_3\text{GeC}_2\text{H}_5$	55-57 (28)		1.4605 (25)		1b	50	156, 188
$(n\text{-C}_7\text{H}_{11}\text{CH}=\text{CH})_3\text{Ge-}n\text{-C}_7\text{H}_{15}$	174 (0.4)		1.4798	0.9194	4		116, 172
$[(\text{CH}_3)_2\text{COHC}\equiv\text{C}]_3\text{GeCH}_3$		208			1b	48	204
$(\text{CH}_2=\text{CH})_2\text{Ge}(\text{C}_2\text{H}_5)_2$	149.8 (760)		1.4575	1.0193	1b	70	100, 142, 156, 188
$(\text{CH}_2=\text{CH})_2\text{Ge}(\text{C}_6\text{H}_5)_2$	111-113 (0.003)				1b	67	85
$(\text{CH}_2=\text{CHCH}_2)_2\text{Ge}(\text{CH}_3)_2$	146 (737)		1.4645	1.0337	1b	42	159
$(\text{CH}_2=\text{CHCH}_2)_2\text{Ge}(\text{C}_6\text{H}_5)_2$	117-120 (0.007)				1b	77	85
$(\text{CH}_2=\text{CHC}_6\text{H}_4)_2\text{Ge}(\text{C}_6\text{H}_5)_2$		139-140			1b	62	145
$[(\text{CH}_3)_2\text{COHC}\equiv\text{C}]_2\text{Ge}(\text{CH}_3)_2$		97			1b	53	204
$[\text{CH}_3\text{COOC}(\text{CH}_3)_2\text{C}\equiv\text{C}]_2\text{Ge}(\text{CH}_3)_2$	142-143 (7)	54			14	57	204
$\text{CH}_2=\text{CHGeH}_3$	-3.5 (760)				13	58.4	29
$\text{CH}_2=\text{CHGeCl}_3$	128.5 (756)		1.4815	1.6527	8	42.7	140, 159
					6		29
$\text{CH}_2=\text{CHGeBr}_3$	55 (7)		1.5883	2.5420	12	73	139
$\text{CH}_2=\text{CHGe}(\text{CH}_3)_3$	70.6 (735)		1.4153	0.9970	1a	38	140
$\text{CH}_2=\text{CHGe}(\text{C}_2\text{H}_5)_3$	151-152 (748)		1.4518	1.0048	1b	35.5	99, 106, 128
$\text{CH}_2=\text{CHGe}(\text{C}_4\text{H}_9)_3$	108-109 (2)		1.4598	0.9479	1b		106, 128
$\text{CH}_2=\text{CHGe}(\text{C}_6\text{H}_5)_3$		62-64			1b	84	85
$n\text{-C}_4\text{H}_9\text{CH}=\text{CHGe}(\text{C}_2\text{H}_5)_3$	102 (10)		1.4623	0.9655	4		116, 172
$n\text{-C}_4\text{H}_9\text{CH}=\text{CHGe}(\text{C}_4\text{H}_9)_3$	102 (10)		1.4798	0.9958	4		116
$\text{C}_6\text{H}_5\text{CH}=\text{CHGeCl}_3$	146-148 (16)		1.5833	1.5328	4	43.5	45
$\text{C}_6\text{H}_5\text{CH}=\text{CHGe}(n\text{-C}_4\text{H}_9)_3$	127 (0.2)		1.5140	1.0221	4	35	116, 172
$\text{C}_6\text{H}_5\text{CH}=\text{CHGe}(\text{C}_6\text{H}_5)_3$		146-149			4	12	84
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CHGe}(n\text{-C}_4\text{H}_9)_3$	98 (0.3)		1.4825	0.9585	9	60	116, 172
$\text{CHCl}=\text{CHGeCl}_3$	164-165 (760)		1.5139	1.7690	8	80	138
$\text{CH}_2=\text{CClGeCl}_3$	151 (753)		1.5002		8	41.6	138
$\text{CF}_2=\text{CFGe}(\text{C}_2\text{H}_5)_3$	45 (10)		1.4138 (25)		1b	40	200
$\text{CF}_2=\text{CFGe}(\text{C}_6\text{H}_5)_3$		84			1b	31.3	200
$\text{CH}_2\text{OHCH}=\text{CHGe}(\text{C}_2\text{H}_5)_3$	112-113 (12)		1.4808	1.0980	4	37	45
$\text{CH}_2\text{OHCH}=\text{CHGe}(n\text{-C}_4\text{H}_9)_3$	105 (0.2)		1.4780	1.0080	4		116, 172
$(\text{CH}_3)_2\text{COHCH}=\text{CHGe}(n\text{-C}_4\text{H}_9)_3$	120 (1)		1.4731	0.9811	4		116, 172
$(\text{CH}_3)_2\text{COHCH}=\text{CHGe}(\text{C}_6\text{H}_5)_3$		90.5-91.5			4	49	84
$(\text{CH}_3)_2\text{COHCH}=\text{C}[\text{COH}(\text{CH}_3)_2]\text{Ge}(\text{C}_2\text{H}_5)_3$	133 (0.6)	70			4	40	116
$\text{CH}_2=\text{CHCH}_2\text{GeH}_3$	37 (752.7)		1.4315	1.0797	13		164
$\text{CH}_2=\text{CHCH}_2\text{GeCl}_3$	155.5 (756)		1.4938	1.5480	5		159
					7	49.5	136, 137
$\text{CH}_2=\text{CHCH}_2\text{GeBr}_3$	205-206 (760)		1.5874	2.3274	5		139
					7	9.4	136
					12	98	139
$\text{CH}_2=\text{CHCH}_2\text{Ge}(\text{CH}_3)_3$	101 (764)		1.4333	0.9952	1a	68.1	159
$\text{CH}_2=\text{CHCH}_2\text{Ge}(\text{C}_2\text{H}_5)_3$	180 (732)		1.4594	1.0004	1a	52.3	159
					7	37	136
$\text{CH}_2=\text{CHCH}_2\text{Ge}(n\text{-C}_4\text{H}_9)_3$	116-117 (2)		1.4664	0.9629	1b		106, 128
$\text{CH}_2=\text{CHCH}_2\text{GeH}(n\text{-C}_4\text{H}_9)_2$	95-96 (13)		1.4608	0.9702	1b		172
$\text{CH}_2=\text{CHCH}_2\text{Ge}(\text{C}_6\text{H}_5)_3$		90-91			1b	59	65
					2	54	201
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{GeCl}_3$	42 (7)				5	24	159
					7	60	136
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Ge}(\text{CH}_3)_3$	121 (733)		1.4416	0.9908	1a	42.5	159
$\text{CH}_2\text{CH}=\text{CHCH}_2\text{GeCl}_3$	177 (759)		1.5080	1.5127	4	61	45
$\text{CH}_2=\text{CHC}_6\text{H}_4\text{Ge}(\text{CH}_3)_3$	39-41 (0.05)		1.5400	1.1060	1b	71	146
$\text{CH}_2=\text{CHC}_6\text{H}_4\text{Ge}(\text{C}_2\text{H}_5)_3$	85 (0.31)		1.5472	1.0740	1b	35	155
					10	26.4	99
$\text{CH}_2=\text{CHC}_6\text{H}_4\text{Ge}(\text{C}_6\text{H}_5)_3$		116-117			1b	67	145
$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}_6\text{H}_4\text{Ge}(\text{CH}_3)_3$	55-57 (0.3)		1.5344	1.0936	1b	57	146

TABLE XV (Concluded)

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
$\text{CH}_2=\text{CHCOOGe}(\text{C}_2\text{H}_5)_3$	85 (10)		1.4480	1.1141	11	60	119
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOGe}(\text{C}_2\text{H}_5)_3$	69-70 (5)		1.4569	1.1439	11	61	101, 110
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOGe}(\text{C}_6\text{H}_5)_2$		86-88			11	25.7	53a
$\text{CH}=\text{CGe}(\text{C}_2\text{H}_5)_3$	70-71 (65)		1.4485	1.0241	1b		106, 124
$\text{CH}=\text{CGe}(n\text{-C}_4\text{H}_9)_3$	105-106 (2.5)		1.4581	0.9602	8	41	106, 124
					1b		124
$\text{C}_3\text{H}_7\text{C}=\text{CGe}(n\text{-C}_4\text{H}_9)_3$	116-117 (0.5)		1.4645	0.9426	1b	69	106, 124
$n\text{-C}_4\text{H}_9\text{C}=\text{CGe}(n\text{-C}_4\text{H}_9)_3$	132 (0.7)		1.4648	0.9381	1b	71	106, 124
$\text{CH}_2=\text{CHCH}_2\text{C}=\text{CGe}(n\text{-C}_4\text{H}_9)_3$	95 (0.2)		1.4723	0.9582	10		106, 125
$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}=\text{CGe}(\text{C}_2\text{H}_5)_2$	97 (23)		1.4792	1.0068	9		125
$\text{C}_2\text{H}_5\text{C}=\text{C}-\text{C}=\text{CGe}(\text{C}_2\text{H}_5)_2$	118 (5)		1.5116	1.0320	1b		106, 125
$(\text{CH}_3)_2\text{COHC}=\text{CGe}(\text{CH}_3)_2$	72-73 (7)	30			1b	45	204
$\text{CH}_2\text{OHC}=\text{CGe}(\text{C}_2\text{H}_5)_2$	112 (9)		1.4822	1.1150	1b	67	45, 106, 125, 203
$(\text{CH}_3)_2\text{COHC}=\text{CGe}(\text{C}_2\text{H}_5)_2$	80 (1)		1.4686	1.0183	10		106, 125
$\text{C}_3\text{H}_7\text{CHOHC}=\text{CGe}(\text{C}_2\text{H}_5)_2$	106 (1)		1.4722	1.0355	1b		203
					10		125
$n\text{-C}_4\text{H}_9\text{OCH}(\text{CH}_3)\text{OCH}_2\text{C}=\text{CGe}(\text{C}_2\text{H}_5)_2$	146-148 (4)		1.4519	1.1130	15	40	203
$n\text{-C}_4\text{H}_9\text{OCH}(\text{CH}_3)\text{OCH}(\text{C}_3\text{H}_7)\text{C}=\text{CGe}(\text{C}_2\text{H}_5)_2$	152-153 (2)		1.4600	1.023	15		203
$\text{CH}=\text{CCH}_2\text{Ge}(\text{C}_2\text{H}_5)_3$	76-77 (18)		1.4669	1.0326	1b	77	124
$\text{CH}_2=\text{CHCH}_2\text{C}=\text{CCH}_2\text{Ge}(\text{C}_2\text{H}_5)_2$	111 (11)		1.4815	1.0295	10		106, 125
$(\text{CH}_2=\text{CH})_2\text{Ge}_2$	55 (0.35-0.25)		1.5217 (25)	1.171 (25)	1b	26.1	188
$(\text{C}_6\text{H}_5\text{CH}=\text{CH})_2\text{Ge}_2$		230-232			3	0.5	24
$(\text{C}_4\text{H}_9)_2\text{GeCH}=\text{CHGe}(\text{C}_4\text{H}_9)_2$	150 (0.2)		1.4798	0.9958	4	90	116, 124, 172
$(\text{C}_2\text{H}_5)_2\text{GeC}=\text{CGe}(\text{C}_2\text{H}_5)_2$	50 (760)				1b		81
$(\text{C}_6\text{H}_{11})_2\text{GeC}=\text{CGe}(\text{C}_6\text{H}_{11})_2$		158			1b		81
$(\text{C}_6\text{H}_5)_2\text{GeC}=\text{CGe}(\text{C}_6\text{H}_5)_2$		127			1b		81
$(\text{C}_6\text{H}_5)_2\text{GeC}=\text{CC}=\text{CGe}(\text{C}_6\text{H}_5)_2$		294			3		82

Properties

The unsaturated organogermanes are in physical appearance and properties much like the alkylgermanes. Vinylgermanes are more stable with respect to cleavage than the corresponding vinyltin compounds. Thus, they are not cleaved by HgCl_2 in refluxing ether and do not undergo redistribution upon heating mixtures of R_4Ge with GeCl_4 (188). Allylgermanes, however, are cleaved by HgCl_2 (128). There are several other differences in reactivity between allyl- and vinylgermanes. Halogens and halogen acids add to vinylgermanes to give the expected product but cleave allylgermanes. Strong carboxylic acids easily cleave the Ge-C bond in both types of compound, but only allyl derivatives are cleaved by formic acid. Trichloroacetic acid cleaves vinyl and 1-acetylenic derivatives slowly, allyl and propargyl derivatives very rapidly. This reagent does not cleave saturated tetrasubstituted germanes (124). Other reagents which cleave the Ge-C bond in unsaturated germanes are trichloroacetic acid and iodine (124, 128).

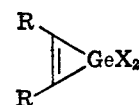
Catalytic hydrogenation of unsaturated organogermanium compounds is more difficult than hydrogenation of the corresponding unsaturated organic compounds and becomes more difficult the nearer the unsaturation to the germanium atom (129). The rate of addition of thiocyanogen to the compounds of the

series $(\text{CH}_3)_3\text{MCH}=\text{CH}_2$ was measured by Bugorkova, Mironov, and Petrov (37). The reactivity of the double bond was found to follow the order $\text{Sn} > \text{Ge} > \text{Si} > \text{C}$.

Trivinyliodogermane is sensitive to light, turning dark red on exposure (188).

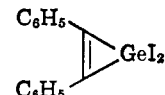
L. GERMIRENES AND GERMOLES

Recently Volpin, Koreshkov, Dulova, and Kursanov (214) reported the successful synthesis of a new class of compounds containing germanium in a three-membered aromatic ring. The general formula for a germirene is



Preparation of Germirenes

Germanium diiodide reacts with diphenylacetylene at 220-230° to form 1,1-diiodo-2,3-diphenylgermirene,



in 30% yield. This reaction competes with the germanium diiodide-catalyzed trimerization of the diphenyl-

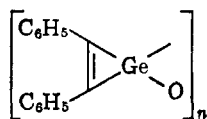
acetylene. In a similar reaction GeI_2 reacts with acetylene at 130–140° under 6 atm. pressure to give 1,1-diiodogermirene in 19.5% yield.

The diiodogermirenes react with NaOH in benzene solution to give the dihydroxy derivatives in high yield. This reaction can be reversed by reacting the hydroxide with hydrogen iodide.

Diphenylgermirene dihydroxide reacts with HBr or HCl in benzene solution to give the halides in 90% yield.

The methyl and ethyl Grignard reagents react with the germirene halides in benzene solution to give the corresponding dialkyl compounds; $(\text{C}_6\text{H}_5)_2\text{C}_2\text{Ge}(\text{CH}_3)_2$, $(\text{C}_6\text{H}_5)_2\text{C}_2\text{Ge}(\text{C}_2\text{H}_5)_2$, and $\text{H}_2\text{C}_2\text{Ge}(\text{CH}_3)_2$ have been prepared in 75–80% yields by this means.

Diphenyldihydroxygermirene dehydrates upon heating to form a polymeric oxide

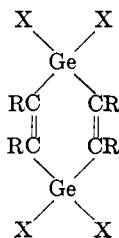


Properties of Germirenes

These compounds are very stable to heat and to the action of bromine, alkali, and strong acids. There is no addition of H_2 to the double bond even in the presence of a platinum catalyst. This suggests that the compounds have an aromatic electronic structure stabilized by conjugation.

Diphenylgermirene diiodide is soluble in chloroform, acetone, and hot benzene, slowly soluble in carbon tetrachloride, and insoluble in heptane, ether, and water. The dihydroxy compound is insoluble in water and most organic solvents. Solubility properties of the remaining germirenes resemble those of diphenylgermirene diiodide (214).

NOTE ADDED IN PROOF.—The structure of the germirenes has been reinvestigated by Johnson and Gohlke. On the basis of mass spectroscopic data and molecular weight determinations, they conclude that these compounds are actually dimeric, the probable structure being



If this structure is correct, the proper name for this class of compounds would be the 1,4-digermins; see F. Johnson and R. S. Gohlke, *Tetrahedron Letters*, 1291 (1962).

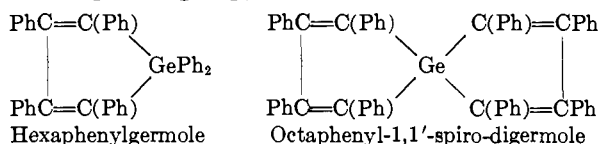
TABLE XVI
GERMIRENES (REFERENCE 214)

Compound	M.p., °C.	Yield, %
$\text{H}_2\text{C}_2\text{GeI}_2$	225–226	19.5
$\text{H}_2\text{C}_2\text{Ge}(\text{OH})_2$		
$\text{H}_2\text{C}_2\text{Ge}(\text{CH}_3)_2$	^a	74.3
$(\text{C}_6\text{H}_5)_2\text{C}_2\text{GeCl}_2$	290–292	89.3
$(\text{C}_6\text{H}_5)_2\text{C}_2\text{GeBr}_2$	317–318	89
$(\text{C}_6\text{H}_5)_2\text{C}_2\text{GeI}_2$	296–298	30
$(\text{C}_6\text{H}_5)_2\text{C}_2\text{Ge}(\text{OH})_2$	600 dec.	82
$[(\text{C}_6\text{H}_5)_2\text{C}_2\text{GeO}]_n$		
$(\text{C}_6\text{H}_5)_2\text{C}_2\text{Ge}(\text{CH}_3)_2$	295	89
$(\text{C}_6\text{H}_5)_2\text{C}_2\text{Ge}(\text{C}_2\text{H}_5)_2$	239–240	78.5

^a Liquid—b.p. 67° (14 mm.), n_D^{20} 1.5009, d_4^{20} 1.2850.

Germoles

The preparation of the germoles, cyclopentadienyl compounds with germanium in the ring, by organolithium synthesis has been described in section II. The structure of these compounds is as follows (Ph represents the phenyl group)



The octaphenyl compound forms yellow needle-like crystals with a melting point of 258–260°. It has not yet been determined whether the five-membered ring has any aromatic character (109a, 109b).

M. ORGANOGERMANIUM COMPOUNDS CONTAINING ALKALI OR ALKALINE EARTH METALS

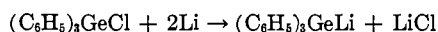
Preparation

1. Cleavage with Na–K Alloy. Hexaphenyldigermane is cleaved by Na–K alloy in the presence of THF. The reaction requires stirring for 24 hr., yields of 65–70% being obtained as determined from the preparation of derivatives (33, 64). Sodium–potassium alloy also cleaves $(\text{C}_6\text{H}_5)_3\text{GeC}(\text{C}_6\text{H}_5)_3$ with formation of the potassium salt. This reaction is much slower (6 days) with only a 28% yield of the carboxylate derivative being obtained (31). Hexamethyldigermane is not cleaved by Na–K alloy in GDME, nor by alkali metals in liquid ammonia (33). For some other unsuccessful cleavage reactions, see Table II, in section III-A.

2. Cleavage with lithium. Hexaphenyldigermane is cleaved by lithium wire to $(\text{C}_6\text{H}_5)_3\text{GeLi}$ in GDME or THF with 3–5 hr. stirring. Yields of 75% can be obtained (62, 210). Under the same conditions tetraphenylgermane is cleaved by lithium wire to form the lithium triphenylgermanide in 70% yield (60). Lithium cleaves triphenylalkylgermanes to split out one of the phenyl groups, forming lithium diphenylalkylgermanide in low yield (68).

3. Metalation using organolithium reagents. Triphenylgermane reacts with C_6H_5Li or $n-C_4H_9Li$ to give lithium triphenylgermanide. This reaction is exothermic in ether solution giving yields of the order of 90%. Methyl lithium in ether solution reacts only on refluxing overnight (63). Metalation of triethylgermane with n -butyllithium or phenyllithium gives lithium triethylgermanide in less than 10% yield (88a).

4. Reaction of lithium with organogermanium halides. A solution of triphenylgermanium bromide in THF stirred 4–5 hr. with lithium wire will give $(C_6H_5)_3GeLi$ in 60% yield (57). The reaction is presumed to go by the following mechanism (210)



A review of the various methods of preparing $(C_6H_5)_3GeLi$ by Tamborski, Ford, Lehn, Moore, and Soloski (210) concluded that cleavage of hexaphenyldigermane is the preferable method. Cleavage of tetraphenylgermane and metalation of triphenylgermanium hydride both result in a mixture of organolithium reagents; metalation of the bromide uses a starting material more difficult to obtain in high purity and gives a lower yield.

5. Metalation using Grignard reagent. Gilman and Gerow (63) have tried to prepare $(C_6H_5)_3GeMgX$ by metalation of triphenylgermane using either the n -butyl or allyl Grignard reagent in refluxing ether. These attempts were unsuccessful. Gilman and Zuech (72) later prepared this compound by reacting either the phenyl or allyl Grignard reagent with triphenylgermane in refluxing THF for two days. However, the Grignard reagents so produced reacted with the THF. Under the same conditions no reaction occurred with the n -butyl Grignard reagent. Attempts to prepare $(CH_3)_3GeMgCl$ by the reaction of trimethylchlorogermane with magnesium have been unsuccessful (188).

6. Side chain Grignard or organolithium reagents. Organogermanium compounds with magnesium (25, 99, 196) or lithium (25, 46) on the side chain have been prepared. The preparation followed the procedures ordinarily used in the synthesis of Grignard or organolithium reagents.

Organic Grignard reagents metalate organogermanium acetylenic compounds in THF to form Grignard reagents of the types: $R_3GeC\equiv CMgBr$ and $R_3GeCH_2C\equiv CMgBr$ (125).

Properties

Suspensions of $(C_6H_5)_3GeK$ in organic solvents have been variously described as orange-red (31), yellow-brown (31), light brown (62), and gray-green (31),

TABLE XVII
ORGANOGERMANIUM COMPOUNDS CONTAINING METALS OF GROUPS
IA AND IIA

Compound	Method of synthesis	Yield, %	References
$(C_2H_5)_3GeLi$	3	10	88a
$(C_6H_5)_3GeLi$	2	75	60, 62, 68, 210
	3	97	63
	4	60	57, 210
$(C_6H_5)_3GeK$	1	83	31, 62
$(C_6H_5)_3GeMgBr$	5	60	72
$(C_6H_5)_2(n-C_{18}H_{37})GeLi$	2	17.6	68
$(C_6H_5)_2(C_6H_5C_2H_4)GeLi$	2	28.6	68
$(C_2H_5)_3Ge-p-C_6H_4Li$	6	90	46
$(CH_3)_3Ge-p-CH_2C_6H_4Li$	6		25
$(CH_3)_3GeCH_2MgCl$	6		25, 196
$(C_2H_5)_3GeC_6H_4MgBr$	6	42.5	99, 155
$(C_2H_5)_3GeC\equiv CMgBr$	6		125
$(n-C_4H_9)_3GeC\equiv CMgBr$	6		125
$(C_2H_5)_3GeCH_2C\equiv CMgBr$	6		125

similarly $(C_6H_5)_3GeLi$ as yellow (63, 210), red-brown (57), and dark brown (60).

Lithium triphenylgermanide metalates fluorene, resulting in fluorene-9-carboxylic acid, but does not react with dibenzofuran (67, 70). The reaction between $(C_6H_5)_3GeLi$ and $(C_6H_5)_3GeCOOCH_3$ results in hexaphenyldigermane, with the elimination of CO_2 , rather than the expected $[(C_6H_5)_3Ge]_2C=O$ (60). The reaction between lithium triphenylgermanide and triphenylgermane gave hexaphenyldigermane in only 12% yield (63).

N. ORGANOGERMYLMETALLIC COMPOUNDS

Preparation

The first four general methods have been used to prepare compounds with germanium-metal bonds or compounds containing both germanium and another metal linked through an organic radical.

1. Grignard reaction.
2. Organolithium synthesis.
3. Wurtz synthesis.
4. Addition of a germanium hydride to a double bond.
5. Reaction of an inorganic oxide with an organogermanium oxide.

The oxides of selenium (181, 185), vanadium, chromium, rhenium (179), arsenic (181), and phosphorus (182), and phosphorus oxychloride (184) react with trimethylgermanium oxide to form compounds in which germanium is bonded to these metals through oxygen. Except for arsenic, phosphorus, and selenium these reactions take place at room temperature. In a similar manner sulfur trioxide and chromium trioxide react with $(CH_3)_3SiOGe(CH_3)_3$ to form $(CH_3)_3SiOSO_2Ge(CH_3)_3$ and $(CH_3)_3SiOCrO_2OGe(CH_3)_3$, respectively (178).

6. Reaction of a silver salt with an organic chloride. The silver salts of the acids corresponding to the six

metallic oxides mentioned above react with trimethylgermanium chloride in nonprotonic solvents to give the same product. With the exception of arsenic the yield is somewhat lower than the oxide reaction (179, 181, 182, 185).

7. Reaction of an inorganic sodium or potassium salt with an organogermanium chloride. When potassium chromate is added to an aqueous solution of dimethylgermanium dichloride, dimethylgermanium chromate is obtained as a precipitate (170).

Schmidt and Ruf (183) prepared trimeric dimethylgermanium selenide by the reaction of sodium selenide with dimethylgermanium dichloride in benzene solution.

The first compounds reported containing germanium-transition metal bonds, $(C_6H_5)_3GeMn(CO)_5$ and $(C_6H_5)_3GeFe(CO)_2(C_6H_5)$, were prepared by the action of the sodium salts $NaMn(CO)_5$ and $Na_2Fe(CO)_2(C_6H_5)$ on triphenylgermanium bromide in THF (192). The preparation of $(C_4H_9)_3GeMn(CO)_5$ and $(C_{18}H_{37})_2Ge[Re(CO)_5]_2$ by the same method has been claimed, but no physical constants were given for these compounds (76).

8. Reaction of alkali-metal siloxanes with organogermanium chlorides. Schmidbaur and Schmidt (176) have prepared the germanosiloxanes, $(CH_3)_3GeOSi(CH_3)_3$ and $[(CH_3)_3SiO]_2Ge(CH_3)_2$, by reacting lithium, sodium, or potassium trimethylsiloxane with the appropriate organogermanium chloride. Reaction with the monochloro compound went to completion at room temperature, the dichloro compound required two hours reflux. Reaction of $(CH_3)_3SiONa$ with $(CH_3)_2GeCl_2$ in 1:1 ratio also gave $(CH_3)_3GeClOSi(CH_3)_3$ which was not isolated as a pure substance.

9. Addition of organotin hydrides to unsaturated organogermanium compounds. This reaction is quite similar to the corresponding reaction of organogermanium hydrides. A number of compounds containing tin and germanium linked through carbon have been prepared by adding di- and triphenylstannane to vinyl (86, 87) and styryl (148) substituted phenylgermanes. The addition of diphenyltin hydride to diphenyldivinylgermane resulted in $(C_6H_5)_3GeCH_2CH_2Sn(C_6H_5)_3$ rather than the expected polymer. Triphenyltin hydride did not add to mono- and diallylphenylgermanes (87). These reactions are carried out at temperatures of 70–90° for 1–6 hr. without catalyst.

10. Triphenylphosphine methylene reacts immediately with triphenylgermanium bromide in ether solution to form the compound $[(C_6H_5)_3GeCH_2P(C_6H_5)_3]Br$. A solution of the crude bromide in methanol upon treatment with sodium tetraphenylborane and precipitation with water gives pure $[(C_6H_5)_3GeCH_2P(C_6H_5)_3]B(C_6H_5)_4$ (187).

11. Triphenylcyclopentadienylgermane upon metalation by butyllithium in ether, followed by reaction with

ferrous chloride or titanium tetrachloride in THF, gives $Fe[C_6H_4Ge(C_6H_5)_3]_2$ and $TiCl_2[C_6H_4Ge(C_6H_5)_3]_2$, respectively (192).

12. $(CH_3)_3GeCH_2MgCl$ reacts with $CH_3Si(OCH_3)_2$ in ether after 15-hr. reflux to give $(CH_3)_3GeCH_2Si(CH_3)(OCH_3)_2$ in 75% yield (196).

13. Trimethylcyanogermane reacts with iron pentacarbonyl in an evacuated tube heated at 75° for 24 hr. to give $(CH_3)_3GeNCFE(CO)_4$ in 69% yield (193).

14. Boric acid reacts with triethylgermane to give triethylgermanium borate, $[(C_2H_5)_3GeO]_3B$, in 50% yield (119). This reaction is another example of the condensation of organogermanium hydrides with hydroxyl compounds (see section F, preparative method 4).

Properties

The two compounds with germanium-boron bonds prepared since 1951, the $[(CH_3)_4N]^+$ and $[(C_6H_5)_3P(CH_3)]^+$ salts of $[(C_6H_5)_3GeB(C_6H_5)_3]^-$, do not have definite melting points and decompose above 200°. The tetramethylammonium salt reacts with bromine to give triphenylbromogermane and tetramethylammonium bromide (195).

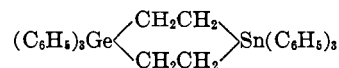
Triphenylgermyltriphenylsilane is cleaved by Na-K alloy in diethyl ether, but not by oxygen in refluxing xylene nor by iodine in refluxing chloroform (63). $(C_6H_5)_3GeSn(C_6H_5)_3$ is cleaved by O_2 in refluxing xylene, by I_2 and organolithium reagents, and by Na-K alloy in the presence of THF initiator (66). (Compare with the data in Table II.)

$(C_6H_5)_3GeMn(CO)_5$ and $(C_6H_5)_3GeFe(CO)_2(C_6H_5)$ are air stable compounds in the solid state but less stable in solution.

The alkylgermanosiloxanes are hydrolyzed in warm water (176). Tetrakis-(triphenylsiloxy)-germane, however, is quite stable to both acid and alkaline hydrolysis (78). $(CH_3)_3GeOSi(CH_3)_3$ is split by $AlCl_3$ and $POCl_3$ at the Ge-O bond (177).

Upon being heated to 100° $(CH_3)_3GeOPOCl_2$ decomposes into trimethylgermanium chloride and polymeric $(PO_2Cl)_x$ (184). Similarly distillation of $[(CH_3)_3GeO_3]VO$ at 106–112° causes decomposition into trimethylgermanium oxide and $[(CH_3)_3GeOVO_2]_x$ (179).

$(CH_3)_3GeOSO_2OSi(CH_3)_3$ (178), $(CH_3)_3GeOCrO_2Si(CH_3)_3$ (178), $[(CH_3)_3GeO]_3AsO$ (181), $[(CH_3)_3GeO]_2SeO_2$ (181, 185), and $[(CH_3)_3GeO]_3VO$ (179) are all hydrolyzed readily by water and $[(CH_3)_2GeSe]_3$ by warm water (183), giving the germanol and the inorganic oxide or its acid.



gives crystalline complexes with 1:1 ratios upon recrystallization from cyclic solvents, such as, benzene, toluene, or dioxane, but not from noncyclic solvents,

TABLE XVIII
 ORGANOGermanium-METAL COMPOUNDS

Compound	B.p. (mm.), °C.	M.p., °C.	n_D^{20}	d_4^{20}	Method of synthesis	Yield, %	References
A. Compounds with metal-metal bonds							
$(C_6H_5)_3GeB(C_6H_5)_3N(CH_3)_4$					2	65	195
$(C_6H_5)_3GeB(C_6H_5)_3P(CH_3)(C_6H_5)_2$					2	65	195
$(C_6H_5)_3GeSi(C_2H_5)_2$		95-96			2	52.5	57, 62
$(C_6H_5)_2GeSi(C_6H_5)_2$	500 (760)	352-353			3	64.1	62
$(C_6H_5)_3GeSn(C_6H_5)_3$		284-286			3	84	60
$[(C_6H_5)_3Ge]_3SiSn(C_6H_5)_3$		340-342			2	60	66
$[(CH_3)_2GeSe]_2$		53			7	15.5	166
$(C_6H_5)_3GeMn(CO)_6$		162-164			7	7	183
$(C_6H_5)_3GeFe(CO)_2(C_6H_5)$	135 (0.001) subl.	160-161			7	40	192
					7	79	192
B. Compounds with metal-oxygen-metal bonding							
$[(C_2H_5)_2GeO]_3B$	128 (0.25)		1.4607	1.1723	14	50	119
$(CH_3)_3GeOSi(CH_3)_3$	116.5-117.5 (723)	-68	1.4038 (18)	0.99	8	70	176, 178
$(CH_3)_2ClGeOSi(CH_3)_3$					8		176
$[(CH_3)_2SiO]_2Ge(CH_3)_2$	165-167 (725)	-61	1.4064		8	69.8	176
$[(C_6H_5)_2SiO]_4Ge$	400 (10^{-4}) subl.	472			8		78
$(CH_3)_3GeOSO_2OSi(CH_3)_3$		92-98			5	99.2	178
$(CH_3)_3GeOCrO_2OSi(CH_3)_3$		-3 to +2			5	91.5	178
$(CH_3)_3GeOPOCl_2$	50-65 (1) subl.	61			5	100	184
$[(CH_3)_3GeO]_3PO$					5		182
					6		182
$[(CH_3)_2GeO]_3AsO$	130-131 (1.5)	46-47			5	37	181
					5	15	181
$[(CH_3)_3GeO]_2SeO_2$	135 (1) subl.	147-148			6	70.1	181, 185
					5	92	181, 185
$[(CH_3)_3GeO]_3VO$	106-112 (1.5) dec.	-18			6	65	179
					5	40	179
$[(CH_3)_3Ge]_2CrO_2$	92-98.5 (1)	61			5	100	179
					6	68	179
$(CH_3)_3GeOReO_4$	115-125 (1.5) subl.	108			5	90	179
					6	77	179
$(CH_3)_2GeCrO_4$		158 dec.			7		170
C. Other compounds							
$(CH_3)_3GeCH_2Si(CH_3)(OCH_3)_2$	65-68 (18)		1.4241 (25)	1.056 (25)	12	75.6	196
$Cl_3GeCH_2CH_2SiCl_3$	120 (15)	35			4	83	158
$Cl_3GeCHClCH_2SiCl_3$	129 (13)		1.5268	1.8350	4	52	158
$(CH_3)Cl_2SiCH_2CH_2GeCl_3$	121.5 (19.5)		1.5025	1.5883	4	67.5	136
$(CH_3)_3GeCH_2CH_2Si(CH_3)_3$	49.5 (13)		1.4363	0.9433	1	80	136
$(C_6H_5)_3GeCF=CFSi(C_6H_5)_3$		64-66			2		199
$Cl_3GeCH_2CH_2CH_2SiCl_3$	107 (4)		1.4503	1.6538	4	97	136
$(C_6H_5)_3GeCH_2CH_2CH_2Si(C_6H_5)_3$		134-135			4	76	131
$(CH_3)_3Ge-p-CH_2C_6H_4Si(CH_3)_3$	108 (5)		1.5067		3	80	25
$(C_2H_5)_3Ge-p-C_6H_4CH_2Si(CH_3)_3$	135-136 (3-4)		1.5088		2	85	47
$(C_2H_5)_3Ge-p-C_6H_4OSi(CH_3)_3$	126-127 (2)		1.5050		3	42	47
$[(CH_3)_3SiC_6H_4]_4Ge$		351-354			2	49	130
$(C_6H_5)_3GeCH_2CH_2Sn(C_6H_5)_3$		210-211			9	32	86
$(C_6H_5)_3GeC_6H_4CH_2CH_2Sn(C_6H_5)_3$		201-203			9	80	148
$(C_6H_5)_2Ge[CH_2CH_2Sn(C_6H_5)_3]_2$		139-142			9	66	86
$(C_6H_5)_2Ge[C_6H_4CH_2CH_2Sn(C_6H_5)_3]_2$		207-209			9	90	148
$(C_6H_5)_2Sn[CH_2CH_2C_6H_4Ge(C_6H_5)_3]_2$		168-169			9	79	148
$(C_6H_5)_2Ge \begin{matrix} \diagup CH_2CH_2 \\ \diagdown CH_2CH_2 \end{matrix} Sn(C_6H_5)_2$		124			9		87, 150
$[(C_6H_5)_3PCH_2Ge(C_6H_5)_3]Br$		121-122			10		191
$[(C_6H_5)_3PCH_2Ge(C_6H_5)_3]B(C_6H_5)_4$		84-85			10		191
$TiCl_2[C_6H_4Ge(C_6H_5)_3]_2$		244 dec.			11		192
$(CH_3)_3GeN=CFe(CO)_4$		69-70			13	69.4	193
$Fe(C_6H_5)[C_6H_4Ge(C_6H_5)_3]$		155-156			1	32	192
					3	10	192
$Fe[C_6H_4Ge(C_6H_5)_3]_2$		244-245			3	38	192
					11		192

such as ethanol. These complexes are weak and decompose on heating (87).

$[(C_6H_5)_3GeCH_2P(C_6H_5)_3][B(C_6H_5)_4]$ is sensitive to sunlight, turning yellow after 30-min. exposure (187).

Trimethylgermylisonitrile-irontetracarbonyl is extremely sensitive to oxygen, decomposes in the absence of air at 120–130°, and is readily soluble in acetone, ether, and chloroform (193).

All of the compounds in Table XVIII are colorless liquids or white crystalline solids with the following exceptions: the compounds containing chromium (170, 178, 179) and the triphenylgermylferrocenyl compounds (192) are orange and $(C_6H_5)_3GeFe(CO)_2$ (C_6H_5) is pale yellow (192).

O. ORGANOGERMANIUM POLYMERS

One class of organogermanium polymers, the oxides, has already been discussed; the remaining types are considered in this section.

Preparation and Properties

1. Polymeric substances formed as by-products. In the preparation of *n*-propylgermanium chlorides by the organolithium method, Johnson and Jones (93) found as a by-product a gel-like solid. Distillation of the petroleum ether extract of this solid gave a liquid whose analysis agreed with the formula $(C_3H_7Ge)_x$. When the reaction was carried out at temperatures above 90°, this became the principal product. Anderson (11) found a solid polymeric material giving the same analysis as a residue in the preparation of isopropylgermanium chlorides using the Grignard reaction.

The action of an alkali metal on trichlorophenylgermane in boiling xylene results in an amorphous substance which was listed in earlier literature as $(C_6H_5Ge)_6$ (91). A reinvestigation of this compound by Metlesics and Zeiss (133) has shown that it can be better represented by the formula $(C_6H_5GeO)_{x-8}$. Bromination of the polymer results in tetrabromodiphenyldigermene, tribromophenylgermane, and dibromodiphenylgermane.

2. Free radical polymerization. Vinylgermane polymerizes readily under the influence of light to form a white solid, $(GeH_2CH_2CH_2)_x$, which is insoluble in organic solvents. This reaction proceeds rapidly in the presence of a trace of mercury (29).

Korshak, Polyakova, Petrov, and Mironov (103, 104) have polymerized a number of vinyl and allyl germanes using free radical polymerization conditions (*t*-butyl peroxide initiator) at 120° under 6000 atm. pressure for 6 hr. The polymers obtained are for the most part oils with a degree of polymerization between three and five. The same group also studied the copolymerization of these substances with methyl methacrylate and styrene under the same conditions and found that the effect of the introduction of alkyl-

germanium units was a reduction of the molecular weight and viscosity of the polymers. Copolymerization of triethylgermanium methacrylate with $HO(CH_2)_6COOH$ results in a product with cross linking, which is accomplished through a side reaction at the metal atoms with splitting out of tetraalkylgermane (102).

Kolesnikov, Davydova, and Klimentova (101) formed polymers of triethylgermanium methacrylate and copolymers with methyl methacrylate and styrene, using benzoyl peroxide and α,α -azobisisobutronitrile (AIBN) as initiators. The germanium polymer had a higher softening temperature than polymethylmethacrylate; copolymerization of the germanium compound with styrene and methyl methacrylate raised the softening temperature of their polymers.

Noltes, Budding, and van der Kerk (146) formed a polymeric solid from $(CH_3)_3Ge-p-C_6H_4CH=CH_2$ using AIBN as initiator. A comparison of the rate of polymerization of this compound with its Group IV analogs, gave as the relative ease of free radical polymerization of Group IV unsaturated compounds: $Pb > Si > C > Ge > Sn$. The same order of relative rates has been found for allyl and vinyl derivatives (104).

3. Ionic polymerization. Kolesnikov, Davydova, and Ermolaeva (100) have studied the polymerization of diethyldiallylgermane using a mixture of triethylaluminum and titanium tetrachloride as an initiator. An oil with molecular weight of 270 (less than a dimer) was obtained. This compound did not undergo free radical polymerization. Attempted polymerization of triethylvinylgermane and 4-triethylgermylstyrene using Friedel-Crafts catalysts, such as titanium tetrachloride, boron trifluoride, or triethylaluminum was unsuccessful, probably due to steric hindrance (99).

4. Hydrolysis. Seyferth and Rochow (198) have formed a cyclic polymer, $[(CH_3)_3GeCH_2Si(CH_3)O]_n$, from $(CH_3)_3GeCH_2Si(CH_3)(OCH_3)_2$ by hydrolysis in a dilute acid solution, and they have prepared copolymers from the product with various siloxanes under conditions of basic hydrolysis. The introduction of organometallic substituents, whether germane or silane, into siloxane polymers results in an increase of viscosity.

The hydrolysis of a mixture of $(CH_3)_2SiCl_2$ and $(CH_3)_2GeBr_2$, followed by treatment with sulfuric acid, results in the formation of a soft rubber-like siloxane-germoxane polymer (208).

5. Polymers formed by addition of a dihydride to double bonds. Noltes and van der Kerk (148, 149, 150) have prepared a number of polymers by the addition of organometallic dihydrides to compounds containing two double or triple bonds. The compounds formed from the addition of organotin dihydride to unsaturated organogermanium compounds have rather low softening temperatures and poor mechanical properties (149). Dibutylgermanium dihydride polym-

TABLE XIX
 ORGANOGERMANIUM POLYMERS

Compound or monomer	Method of prepn.	Reaction conditions	Yield, %	State	Mol. wt.	Physical properties	References			
A. Polymers formed as by-products										
$(n-C_8H_7Ge)_n$	1			Liquid			93			
$(i-C_8H_7Ge)_n$	1			Solid			11			
B. Polymers formed from organogermanium monomers (monomer)										
$CH_3Ge(CH_2CH=CH_2)_2$	2	120°, 6 hr., <i>t</i> -butyl peroxide	38.6	Oil	780 $n = 3.7$		103			
$CH_3Ge(CH_2CH=CH_2)_3$	2	6000 atm., 120°, 6 hr., <i>t</i> -butyl peroxide	100	Glass	Trimer		103			
$(C_2H_5)_2Ge(CH=CH_2)_2$	2	6000 atm., 120°, 6 hr., <i>t</i> -butyl peroxide	100	Glass			104			
$(CH_3)_2Ge(CH_2CH=CH_2)_2$	2	6000 atm., 120°, 6 hr., <i>t</i> -butyl peroxide	100	Solid	Trimer		103			
$(C_2H_5)_2Ge(CH_2CH=CH_2)_2$	3	60°, 8 hr., $Et_3Al:TiCl_4$	50	Oil	270		100			
$CH_2=CHGeH_2$	2	Hg-light catalyzed		Solid		275° dec.	29			
$(CH_3)_2GeCH=CH_2$	2	6000 atm., 120°, 6 hr., <i>t</i> -butyl peroxide	35.1	Oil	747 $n = 5$		104			
$(CH_3)_2GeCH_2CH=CH_2$	2	6000 atm., 120°, 6 hr., <i>t</i> -butyl peroxide	34	Oil	560 $n = 3.5$		103			
$(C_2H_5)_2GeCH_2CH=CH_2$	2	6000 atm., 120°, 6 hr., <i>t</i> -butyl peroxide	64.4	Oil	780 $n = 3.9$		103			
$(CH_3)_2Ge-p-C_6H_4CH=CH_2$	2	70-90°, 10 hr., AIBN		Solid		Softens 170-180°	146			
$(C_2H_5)_2GeOCCC(CH_3)=CH_2$	2	Benzoyl peroxide	10	Solid		$[\eta] = 0.85$	101			
$(C_2H_5)_2GeOCCC(CH_2)=CH_2$	2	AIBN	100	Solid	200,000	$[\eta] = 0.50$	101			
$(CH_3)_2GeCH_2Si(CH_3)(OCH_3)_2$	4	Stirred 12 hr.		Liquid		b.p. 90° (0.45 mm.) $n_D^{25} 1.4640$ $d_4^{25} 1.194$	139			
Component A— mole %	Component B— mole %	Method of prepn.	Reaction conditions	Yield, %	Ratio in product, A:B	State	Mol. wt.	Physical properties	References	
C. Copolymers										
$(n-C_4H_9)_2GeH_2$	50	$HC=CCH_2CH_2C=CH$	50	5	80-120°, 8 days, chloroplatinic acid	1:1	Rubber		149	
$(C_6H_5)_2GeH_2$	50	$HC=CCH_2CH_2C=CH$	50	5	80-120°, 8 days, chloroplatinic acid	1:1	Oil	10,000 Very viscous	149	
$(CH_3)_2GrBr_2$	5	$(CH_3)_2SiCl_2$	95	4	5-10°	2:98	Oil		145	
$(CH_3)_2Ge(CH=CH_2)_2$	50	$(CH_3)_2SiHOSiH(C_2H_5)_2$	50	5	120°, 6 hr., chloroplatinic acid	1:1	Oil	4447 $n = 13$	105	
$(C_2H_5)_2Ge(CH=CH_2)_2$	50	$(CH_3)_2SiHOSiH(C_2H_5)_2$	50	5	120°, 6 hr., chloroplatinic acid	1:1	Oil	6209 $n = 15$	105	
$(C_2H_5)_2Ge(C_6H_5-CH=CH_2)_2$	50	$(n-C_4H_9)_2SnH_2$	50	5	75-115°, 39 hr.	1:1	Solid		150	
$(C_2H_5)_2Ge(C_6H_5-CH=CH_2)_2$	50	$(n-C_4H_9)_2SnH_2$	50	5	75-115°, 39 hr.	1:1	Solid		150	
$(C_2H_5)_2Ge(C_6H_5-CH=CH_2)_2$	50	$(C_6H_5)_2SnH_2$	50	5	75-115°, 39 hr.	1:1	Glass	27,000 $n = 45$	Softened 105-110° 148, 150	
$(CH_3)_2GeCH_2-CH=CH_2$	29	$CH_2=C(CH_3)-COOCH_3$	71	2	6000 atm., 120°, 6 hr., <i>t</i> -butyl peroxide	1:53	Solid	$[\eta] = 1.54$	103	
$(CH_3)_2GeCH_2-CH=CH_2$	17	$C_6H_5CH=CH_2$	83	2	120°, 6 hr., <i>t</i> -butyl peroxide	1:116	Solid	$[\eta] = 0.343$	104	
$(CH_3)_2GeCH_2-CH=CH_2$	17	$C_6H_5CH=CH_2$	83	2	6000 atm., 120°, 6 hr., <i>t</i> -butyl peroxide	1:69	Solid	$[\eta] = 0.336$	103	
$(C_2H_5)_2GeCH_2-CH=CH_2$	27	$CH_2=C(CH_3)-COOCH_3$	73	2	6000 atm., 120°, 6 hr., <i>t</i> -butyl peroxide	1:13	Solid	$[\eta] = 1.74$	103	
$(CH_3)_2GeCH_2-C(CH_3)=CH_2$	20	$CH_2=C(CH_3)-COOCH_3$	80	2	6000 atm., 120°, 6 hr., <i>t</i> -butyl peroxide	1:46			103	
$(C_2H_5)_2GeOCCC-(CH_3)=CH_2$	20	$C_6H_5CH=CH_2$	80	2	AIBN	7:93	Solid	$[\eta] = 0.28$	101	
$(C_2H_5)_2GeOCCC-(CH_3)=CH_2$	20	$CH_2=C(CH_3)-COOCH_3$	80	2	Benzoyl peroxide	1:195	Solid	$[\eta] = 0.45$	101	
$[(CH_3)_2GeCH_2Si(CH_3)O]_n$		$(CH_3)_2Si_2O$	4	4	Reflux 12.5 hr.	38.8	1:1	Liquid	359 $n = 1$ $\eta = 2.14$ cp. (25°) b.p. 56-58° (0.3 mm.) $n_D^{25} 1.4200$, $d_4^{25} 0.972$	198
$[(CH_3)_2GeCH_2Si(CH_3)O]_n$		$(CH_3)_2Si_2O$	4	4	Reflux 12.5 hr.	17.0	1.6:1	Liquid	472 $\eta = 4.22$ cp. (25°) b.p. 74-110° (0.2 mm.) $n_D^{25} 1.4330$ $d_4^{25} 1.036$	198
$(CH_3)_2SiOSi(CH_3)-[CH_2Ge-(CH_3)_2]OSi(CH_3)_2$	50	$[(CH_3)_2SiO]_n$	50	4	Reflux 10.5 hr.	43.5	1:5.6	Liquid	766 $\eta = 26.72$ cp. (25°) $n_D^{25} 1.4268$, $d_4^{25} 1.051$	198

erizes to a lesser extent with hexadiyne than does the corresponding organotin compound; it also requires longer reaction times and the use of chloroplatinic acid catalyst (150).

The siloxane dihydride, $(CH_3)_2SiH-O-HSi(C_2H_5)_2$, adds to the double bonds in dimethyl- and diethyl-

divinylgermane, using chloroplatinic acid catalyst, to form polymeric oils with a degree of polymerization between 13 and 15 (105). Diphenylgermane adds to diethyldivinylgermane to give both a cyclic compound (see section II-H) and a viscous polymeric liquid (127).

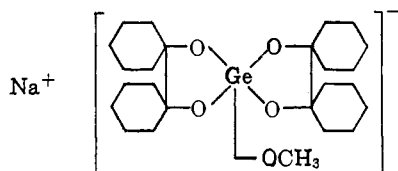
P. ORGANOGERMANIUM COMPOUNDS WITH
HIGHER COÖRDINATION NUMBERS

Acetylacetonyl Compounds

Up to 1951, seven germanium compounds with a coördination number of six were known. These were the three germanium bisacetylacetonate dihalides, the two germanium trisacetylacetonate copper halides, and germanium bispropionylacetonate dichloride (91). Only one new compound of this type has been prepared, trisacetylacetonategermanium iron tetrachloride, $[\text{CH}(\text{C}-\text{CH}_3\text{O})_2]_3\text{GeFeCl}_4$, which was synthesized by the reaction of acetylacetonate, germanium tetrachloride, and ferric chloride in chloroform. This compound is a yellow-green crystalline substance (143).

Sodium Methylate Addition Compound

Bis-(cyclohexyl-1,1'-dioxy)-germane reacts with sodium methylate to form a precipitate in which the germanium atom is apparently five-coördinate. The structure proposed for this compound is (143)



Phthalocyanines

A series of 6-coördinate germanium compounds has recently been prepared in which four of the coördination positions of germanium are taken up by the phthalocyanine molecule and the remaining two by functional groups (95, 96).

The parent compound of this series, dichlorogermanium phthalocyanine, has been prepared by three methods: the reactions of germanium tetrachloride with phthalonitrile in refluxing quinoline (method 1); *o*-cyanobenzamide in refluxing 1-chloronaphthalene (method 2); and phthalocyanine in refluxing quinoline (method 3). The third method gives the highest yield (95, 96).

Hydrolysis of the dichloride in refluxing pyridine-ammonia solution or concentrated sulfuric acid gives dihydroxygermanium phthalocyanine. Hydrolysis was slow in water, concentrated ammonia, and live steam (95).

The dihydroxy compound reacts with phenols and silanols in refluxing benzene to give the diphenoxy-, bis-(*p*-phenylphenoxy)-, bis-(triphenylsiloxy)- (95), and bis-(diphenylhydroxysiloxy)- (96) germanium phthalocyanine compounds in high yield.

The crude bis-(diphenylhydroxysiloxy) compound reacts with refluxing dioxane to give bis-(diphenylhydroxysiloxy)-germanium phthalocyanine bisdioxanate, and with refluxing benzyl alcohol to give bis-

(diphenylbenzyloxysiloxy)-germanium phthalocyanine. The same compound, when heated at 385° under vacuum gives a polygermanosiloxane phthalocyanine complex (96).

All of these compounds are crystalline and appear blue-green in transmitted light, reddish in reflected light. Because of the bulky nature of the siloxy groups, a *trans* configuration for these compounds is indicated. Since the siloxy compounds are derived directly from the hydroxy compound, the *trans* configuration of the whole series can be assumed (95, 96).

TABLE XX
ORGANOGERMANIUM COMPOUNDS WITH FIVE OR SIX
COÖRDINATION

Compound	M.p., °C.	Subl. pt., °C. (μ)	Yield, %	Refer- ence
$(\text{CH}_3\text{COC}=\text{C}(\text{CH}_3)\text{CO})_2\text{GeFeCl}_4$	184		42.4	143
$(\text{C}_{12}\text{H}_{20}\text{O})_2\text{GeOCH}_2\text{Na}^a$				143
$\text{C}_{22}\text{H}_{18}\text{N}_8\text{GeCl}_2^b$		450-60 (2)	(1) 50 (2) 18.1 (3) 78.8	95 96 96
$\text{C}_{22}\text{H}_{18}\text{N}_8\text{Ge}(\text{OH})_2$			100	95
$\text{C}_{22}\text{H}_{18}\text{N}_8\text{Ge}(\text{OC}_6\text{H}_5)_2$		385 (2)		95
$\text{C}_{22}\text{H}_{18}\text{N}_8\text{Ge}[\text{OC}_6\text{H}_4\text{C}_6\text{H}_5]$		355 (2)		95
$\text{C}_{22}\text{H}_{18}\text{N}_8\text{Ge}[\text{OSi}(\text{C}_6\text{H}_5)_2]_2$		390 (2)		95
$\text{C}_{22}\text{H}_{18}\text{N}_8\text{Ge}[\text{OSi}(\text{C}_6\text{H}_5)_2\text{OH}]_2$				96
$\text{C}_{22}\text{H}_{18}\text{N}_8\text{Ge}[\text{OSi}(\text{C}_6\text{H}_5)_2\text{OH}]_2 \cdot 2-$ $(\text{C}_6\text{H}_5\text{O}_2)$				96
$\text{C}_{22}\text{H}_{18}\text{N}_8\text{Ge}[\text{OSi}(\text{C}_6\text{H}_5)_2\text{OCH}_2\text{C}_6\text{H}_5]_2$				96

^a Bis-(cyclohexyl-1,1'-dioxy)-germane sodium methylate. ^b $\text{C}_{22}\text{H}_{18}\text{N}_8$, phthalocyanine.

IV. SPECTRAL STUDIES OF ORGANOGERMANIUM
COMPOUNDS

A. MICROWAVE SPECTRA

Several studies of the microwave spectrum of methylgermane have been made (19, 20, 109). The physical constants calculated from these studies are included in Table XXI. The only other microwave spectrum published is that of methyltrichlorogermane for which the molecular parameters were not calculated (89).

TABLE XXI
MOLECULAR CONSTANTS FOR METHYLGERMANE

	Laurie (109)	Barchukov and Prokhorov (20)
$r(\text{C}-\text{H})$	$1.083 \pm 0.005 \text{ \AA.}$	1.09 \AA.
$r(\text{Ge}-\text{C})$	$1.9453 \pm 0.0005 \text{ \AA.}$	$1.946 \pm 0.001 \text{ \AA.}$
$r(\text{Ge}-\text{H})$	$1.529 \pm 0.005 \text{ \AA.}$	1.53 \AA.
$\angle\text{H}-\text{C}-\text{H}$	$108^\circ 25'$	$107^\circ 39'$
$\angle\text{H}-\text{Ge}-\text{H}$	$109^\circ 15'$	$108^\circ 10'$
Dipole moment	$0.635 \pm 0.006 \text{ D.}$	$0.67 \pm 0.02 \text{ D.}$ $0.644 \pm 0.006 \text{ D (19)}$

B. INFRARED AND RAMAN SPECTRA

The frequency of some characteristic infrared vibrations of organogermanium compounds are listed in Table XXII. Extensive studies of the effect of various substituents on the frequency of the Ge-H absorption have been made at the Faculty of Science, Toulouse

TABLE XXII

CHARACTERISTIC FREQUENCIES OF ORGANOGermanium COMPOUNDS—INFRARED AND RAMAN

Group	Frequencies, cm. ⁻¹	Compounds studied	References
Ge—H (R ₃ GeH)	1980–2040	13 compounds	55, 122, 163, 172, 174, 216
Ge—H (R ₃ GeH ₂)	2030–2060	7 compounds	122, 163, 172, 174, 216
Ge—H (RGeH ₃)	2062–2065	7 compounds	122, 163, 172, 174
	2085, 2100	CH ₂ =CH ₂ GeH ₃	29
Ge—Br	309	(C ₆ H ₅) ₃ GeBr	26
Ge—C (methyl, ethyl)	550–572	9 compounds	32, 34, 110, 120, 121, 140
Ge—Cl	397, 425	C ₂ H ₅ GeCl ₂	120
	376, 395	(C ₂ H ₅) ₂ GeCl ₂	120
	377	(C ₆ H ₅) ₃ GeCl	26
Ge—Ge	273 (stretching)	(CH ₃) ₆ Ge ₂	32
	210 (bending)	(C ₂ H ₅) ₆ Ge ₂	80
Ge—O (alkoxide)	1040	7 compounds	92
Ge—O (oxide)	670–700		
	800–900	Methyl, phenyl oxides	34, 134
Some frequencies of functional groups in organogermanium compounds			
C=C (vinyl)	1594–1610	6 compounds	123, 140
C=C (allyl)	1625–1630	4 compounds	51, 123
C≡C(H) (α)	2027	(C ₂ H ₅) ₂ GeC≡CH	123
		(C ₆ H ₅) ₂ GeC≡CH	
		(C ₂ H ₅) ₂ GeCH ₂ C≡CH	123
C≡C(H) (β)	2100	CH	
C≡C(R) (α)	2146–2169	6 compounds	123
C—H (vinyl)	3000	4 compounds	123, 140
	3040–3055		
	3025–3033		
C—H (allyl)	3056–3058	4 compounds	51, 123
	3075–3080		
=CH ₂ (vinyl)	940–950	4 compounds	123, 140
	1000–1010		
	1400		
=CH ₂ (allyl)	930	4 compounds	51, 123
	990–995		
	1425–1430		
≡CH (α)	3290, 3276	See above	123
≡CH (β)	3310, 3304	See above	123
Phenyl deformation	1080	8 compounds	85, 86, 147

(122, 172, 174), and at the N. D. Zelinski Institute for Organic Chemistry, Moscow (163, 164). The effect of the germanium atom on the frequency of absorption of unsaturated groups also has been studied (123).

Complete assignments of vibrational frequencies have been made in the Raman spectra of tetramethylgermane (121, 205), hexamethyldigermane (32), ethyltrichlorogermane (120), and diethyldichlorogermane (120) and in the infrared spectra of tetramethylgermane (121), vinylgermane (29), and dimethyldiperfluorovinylgermane (206). From the Raman spectra, the force constant of the Ge—C bond has been calculated to be 2.76×10^{-5} dynes/cm. in tetramethylgermane and 2.57×10^{-5} dynes/cm. in hexamethyldigermane; the Ge—Ge force constant in hexamethyldigermane is 1.34×10^{-5} dynes/cm. (32).

C. ULTRAVIOLET AND VISIBLE SPECTRA

Absorption in the visible and near-ultraviolet have been used to follow cleavage reactions of trialkylarylgermanes and in the titration of organogermanium carboxylic acids (25, 48, 49, 50); however, the absorption spectra of only five compounds have been reported.

TABLE XXIII

SPECTRA OF ORGANOGermanium COMPOUNDS IN THE ULTRAVIOLET AND VISIBLE REGIONS

Compound	λ_{\max} (m μ)	Reference
Absorption spectra		
(C ₆ H ₅) ₄ Ge	269, 265, 262, 259, 253, 247, 244	107
(C ₆ H ₅) ₆ Ge ₂	239	79
(C ₆ H ₅) ₃ Ge- <i>p</i> -C ₆ H ₄ CONH ₂	238 (261, 274, 284) ^a	165
(C ₆ H ₅) ₃ Ge- <i>p</i> -C ₆ H ₄ COOH	238 (264, 269, 276, 284) ^a	165
(C ₆ H ₅) ₃ Ge- <i>m</i> -C ₆ H ₄ COOH	252, 258, 265, 276, 284	165
Emission spectrum		
(C ₆ H ₅) ₄ Ge	320, 450, 470, 510	107
^a Not very well defined.		

Absorption maxima for these compounds are listed in Table XXIII. On the basis of their absorption and emission spectra, the electronic structure (107) and singlet-triplet transitions (108) of the Group IV tetraphenyls have been discussed by LaPaglia.

D. NUCLEAR MAGNETIC RESONANCE SPECTRA

The hydrogen nuclear magnetic resonance spectra of tetramethylgermane (2, 36, 213), hexamethyldigermane (36), and trimethylgermanium oxide (36) have been obtained. Allred and Rochow (2) have used the relative chemical shifts in the tetramethyl derivatives of the Group IV elements as the basis of an electronegativity scale. The ¹⁹F spectra of triethylperfluorovinylgermane (200), dimethyldiperfluorovinylgermane (41), and tetraerfluorovinylgermane (41) have been investigated, and the F—F coupling constants for these compounds calculated.

E. MASS SPECTROSCOPY

The mass spectra of the Group IV tetramethyls has been determined by Dibeler (43). The abundance of ions resulting from the dissociation of methyl groups increases with increasing atomic number of the central atom. The relative abundance of the various ions found in the spectrum suggests that ionization occurs by loss of a bonding electron between the central atom and a methyl group.

The electron-impact spectrum of tetramethylgermane has been determined by Hobrock and Kiser (88). The appearance potential of the various ions was obtained and their heats of formation calculated assuming a value of -35 kcal./mole for the heat of formation of tetramethylgermane. The ionization potential of tetramethylgermane was found to be 9.2 electron volts.

The authors wish to acknowledge the financial support received from the United States Atomic Energy Commission under Contract AT(11-1)-38 and from the Research Corp. We also want to thank the other members of our research group for their help in the preparation of the manuscript.

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