Chem., 3, 1456 (1964).
230. R.E.Enrione, F.P.Boer, and W.N.Lipscomb, Inorg.Chem., 3, 1659 (1964).
231. H.A.Beall and W.N.Lipscomb, Inorg.Chem., 3, 1783 (1964).
232. Q.Johnson, R.Schaeffer, and G.Smith, Inorg.Chem., 4, 917 (1965).
233. R.E.Williams and F.J.Gerhart, J.Amer.Chem.Soc., 87, 3513 (1965).
234. E.L.Muetterties and W.H.Knoth, Inorg.Chem., 4, 1498 (1965).

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COVALENT ORGANODIELEMENTARY COMPOUNDS

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I. INTRODUCTION

Among organodielementary compounds we include compounds containing, apart from the usual elements (C, H, O, N, Cl, etc.), two inorganic elements. When the latter are metals, the compounds will be termed organodimetallic compounds.

In organodielementary compounds the inorganic elements may be separated by hydrocarbon groups or may be adjacent to one another. In the latter case the bond between them may be either ionic or covalent. Razuvaev and his coworkers are playing an active part in developing methods for the synthesis of organodielementary compounds having a covalent bond between the inorganic elements and also in examining their reactivity. The present paper reviews work in this field and is based on the literature up to May 1965. Investigations on organodielementary compounds having an ionic bond between the inorganic elements have been discussed several times in reviews and monographs [1-5].

II. METHODS OF PREPARATION

Organodielementary compounds containing an M–M' bond (here and below M and M' denote the inorganic elements) are usually prepared by reaction of R_3SiLi and analogous compounds with inorganic or organoelementary halides (method A), e.g.

$$(C_6H_5)_3SiK + (C_6H_5)_3SnCl \longrightarrow KCl + (C_6H_5)_3SiSn(C_6H_5)_3, \quad (1)$$

$$3(C_6H_5)_3GeNa + SiHCl_3 \longrightarrow [(C_6H_5)_3Ge]_3SiH + 3NaCl. \quad (2)$$

The yield of triphenyltriphenylsilyltin from reaction (1) is 76%;[6] tristriphenylgermylsilane is formed in quantitative yield in conformity with Eqn. (2).[7]

Method A has been used to synthesise several compounds containing Si–Ge,[6,8-12] Si–Sn,[7,13-16] Ge–Sn[17,18], Ge–Pb[18], and Sn–Pb[18] groups. Covalent organotrielementary compounds have been obtained in a similar manner[1]:

$$[(C_6H_5)_3Ge]_3SiLi + ClSn(C_6H_5)_3 \longrightarrow [(C_6H_5)_3Ge]_3SiSn(C_6H_5)_3 + LiCl.$$

In 1964 this method was used to synthesise a series of organodimetallic compounds having a neopentane configuration of metal atoms[18-21]:

$$4(C_6H_5)_3MLi + M'Cl_4 \longrightarrow [(C_6H_5)_3M]_4M' + 4LiCl,$$

$$4(C_6H_5)_3MLi + 2PbCl_2 \longrightarrow [(C_6H_5)_3M]_4Pb + Pb + 4LiCl,$$

where M = Pb, Sn and M' = Sn, Ge.

The attempt to obtain tetrakistriphenylgermyltin from triphenylgermyl-lithium and tin tetrachloride was unsuccessful[18], since in this case metal–halogen exchange predominates, with the formation of hexaphenyldigermane:

$$(C_6H_5)_3GeLi + SnCl_4 \longrightarrow (C_6H_5)_3GeCl + [LiSnCl_3],$$

$$(C_6H_5)_3GeCl + (C_6H_5)_3GeLi \longrightarrow LiCl + (C_6H_5)_6Ge_2.$$

This work showed that, in the synthesis of compounds of the type $[(C_6H_5)_3M]_4M'$ the tendency for metal–halogen exchange to occur diminishes in the sequence

$$(C_6H_5)_3GeLi > (C_6H_5)_3SnLi > (C_6H_5)_3PbLi.$$

The occurrence of this secondary process, which often leads to the formation of difficultly separable mixtures of products[8,17], is a substantial disadvantage of method A. Thus the interaction of $(C_6H_5)_3GeK$ with $(C_6H_5)_3SiCl$, for example, yields a difficultly separable mixture containing $(C_6H_5)_6Ge_2$, $(C_6H_5)_6Si_2$, and $(C_6H_5)_3GeSi(C_6H_5)_3$.[8,17] The attempt to prepare $(C_6H_5)_3SnSi(CH_3)_3$ from $(CH_3)_3SiCl$ and $(C_6H_5)_3SnLi$ failed, since in this system metal–halogen exchange and its accompanying processes occur preferentially[14]:

$$(C_6H_5)_3SnLi + (CH_3)_3SiCl \longrightarrow (C_6H_5)_3SnCl + (CH_3)_3SiLi,$$

$$(C_6H_5)_2SnCl + (C_6H_5)_3SnLi \longrightarrow LiCl + (C_6H_5)_6Sn_2 \text{ (yield 69\%)},$$

$$(CH_3)_3SiLi + (CH_3)_3SiCl \longrightarrow LiCl + (CH_3)_6Si_2.$$

Blake et al. have made the interesting observation that the interaction of $(CH_3)_3SiCl$ with $(C_4H_9)_3SnLi$ is preceded by dissociation of the latter compound[22]:

$$(C_4H_9)_3SnLi \rightleftarrows (C_4H_9)_2Sn + C_4H_9Li,$$

$$C_4H_9Li + (CH_3)_3SiCl \longrightarrow LiCl + (CH_3)_3SiC_4H_9,$$

the yield of butyltrimethylsilane being 54%. Such a process is not characteristic of the reaction of triphenylstannyl-lithium with triphenylchlorosilane[14].

Method A has been employed also for the synthesis of organodielementary compounds containing Si–Hg bonds. Attempts to use the reaction of triphenylsilyl-lithium with mercury halides, phenylmercuric chloride, or diphenylmercury were unsuccessful[23]. It was therefore supposed

that the Si–Hg bond in organosilicon compounds of mercury was unstable. This conclusion was subsequently disproved by the work of Wiberg [15], Razuvaev [24,25], and their coworkers. Wiberg, in particular, synthesised by method A triphenylsilyl derivatives of mercury, zinc, and aluminium:

$$n\,(C_6H_5)_3SiK + MCl_n \longrightarrow [(C_6H_5)_3Si]_nM + n\,KCl,$$

where M = Hg, Zn, Al and n = 2, 3. He showed also that interaction of R_3SnLi with chlorotrimethylsilane or a dialkyldichlorosilane in ether at -20° gives yields of up to 60–70% of compounds of types $R_3SnSi(CH_3)_3$ and $(R_3Sn)_2SiR'_2$, where R = C_2H_5, C_4H_9, C_6H_5 and R′ = CH_3, C_6H_5.

The method was further developed by Schumann and Schmidt [26], who achieved the reaction

$$3\,(C_6H_5)_3SnLi + MCl_3 \longrightarrow [(C_6H_5)_3Sn]_3M + 3LiCl,$$

where M = As, Sb, Bi. The yield of the required products is ~80%. The chloride MCl_3 can be replaced by mixed organometallic compounds R_2MCl. In this way these workers obtained compounds containing one Sn–As covalent bond. The first representative of this class of compounds, diphenyltrimethylstannylarsine, had been obtained previously by a different method [27]. For the synthesis of compounds of the $R_3SnM(C_6H_5)_2$ series, where R = CH_3, C_2H_5, C_3H_7, C_4H_9 and M = As, Sb, see also Ref. 28. The infrared spectra of compounds containing covalent Sn–As and Sn–Sb bonds are discussed in Ref. 29.

Repeated attempts have been made to use method A [23,30] for the synthesis of compounds containing an Si–Bi, Si–Hg, Si–Cd, or Si–Zn bond. The reactions of triphenylsilyl--lithium with metal halides have been studied for this purpose. In the $(C_6H_5)_3SiLi$–$BiCl_3$ system the predominant reaction is metal–halogen exchange, leading to the formation of hexaphenyldisilane [30]. In some cases, nevertheless, the intermediate formation of organodielementary compounds is assumed [23] (e.g. in the reactions with mercury, lead, and tin halides). For the occurrence of unstable compounds containing an Si–P, Si–As, or Si–Sb bond in the reactions of triphenylsilyl-lithium with halides of Group V elements see Ref. 31.

Method A has been employed also for the synthesis of organodielementary compounds containing an Sn–P [32–34], Sn–Ti [35], Sn–B [36], or Pb–Ti [35] bond. There is no doubt that its synthetic possibilities have not yet been completely exhausted.

In 1963 Razuvaev and his coworkers began to apply the reaction of alkylated hydrides of Group IV elements with organometallic compounds to the synthesis of compounds containing covalent M–M′–M bonds (method B) [24,25,37–44]. The yield of organodielementary compounds is usually high:

$$n\,(C_2H_5)_3MH + (C_2H_5)_nM' \longrightarrow n\,C_2H_6 + [(C_2H_5)_3M]_nM',$$

where

M=Ge, Si;	M′=Hg, Cd, Zn;	n=2
M=Ge, Sn;	M′=Se;	n=2
M=Ge, Si;	M′=Tl;	n=3
M=Ge, Si, Sn;	M′=Bi, Sb;	n=3

Bistriethylgermylmercury was obtained at the same time, independently, and by the same reaction by Neumann and Kühlein [45]. These workers established [46,47], however, that method B can be used to synthesise complicated organodielementary compounds containing chains of inorganic elements, e.g.

$$4\,(C_6H_5)_2GeH_2 + 4\,(C_2H_5)_2Hg \longrightarrow 8C_2H_6 + 4/n\,[-(C_6H_5)_2GeHg-]_n \xrightarrow{h\nu} [(C_6H_5)_2Ge]_4 + [(C_6H_5)_2Ge]_n + 4Hg. \quad (3)$$

In 1964 method B was employed for the synthesis of bistriphenylstannyl sulphide [48]:

$$2\,(C_6H_5)_3SnH + (C_6H_5CH_2)_2S \longrightarrow 2C_6H_5CH_3 + [(C_6H_5)_3Sn]_2S.$$

Vyazankin et al. found that triethylsilane [24] and pentaethyldisilane [25] react with diethylmercury to form mainly products containing Si–Hg–C groupings:

$$R\,(C_2H_5)_2SiH + (C_2H_5)_2Hg \longrightarrow C_2H_6 + R\,(C_2H_5)_2SiHgC_2H_5, \quad (4)$$

where R = C_2H_5, $(C_2H_5)_3Si$. The yield of the symmetrical products — bistriethylsilylmercury and bis(pentaethyldisilanyl)mercury — was only 3.3% and 8.1% respectively. This has permitted the synthesis of triethylgermyl(triethylsilyl)mercury (26.2%) and of pentaethyldisilanyl(triethylgermyl)mercury (50.4%), which are the first organotrielementary compounds containing an Si–Hg grouping:

$$(C_2H_5)_3GeH + C_2H_5HgR \longrightarrow C_2H_6 + (C_2H_5)_3GeHgR, \quad (5)$$

where R = $(C_2H_5)_3Si$, $(C_2H_5)_3SiSi(C_2H_5)_2$.

It follows from Eqns. (4) and (5) that triethylgermane is more reactive than triethylsilane. This is confirmed by reactions (6)–(8), which constitute a further development of method B and from which it can be concluded that the reactivity of the hydrides in the above processes decreases in the sequence

$$(C_2H_5)_3SnH > (C_2H_5)_3GeH > (C_6H_5)_3SiH > (C_3H_7)_3SiH \simeq (C_2H_5)_3SiH \text{ [44]}:$$

$$(C_2H_5)_2SnH + [(C_2H_5)_3Ge]_3M' \longrightarrow (C_2H_5)_3GeH + [(C_2H_5)_3Sn]_3M', \quad (6)$$

$$(C_2H_5)_3GeH + [(C_2H_5)_3Si]_3M' \longrightarrow (C_2H_5)_3SiH + [(C_2H_5)_3Ge]_2M', \quad (7)$$

$$(C_6H_5)_3SiH + [(C_2H_5)_3Si]_3M' \rightarrow (C_2H_5)_3SiH + [(C_6H_5)_3Si]_3M', \quad (8)$$

where M′ = Bi, Sb.

Reaction (8) does not go to completion even under very severe conditions (230° for 20 h). The yield of hydrides and of the corresponding organodimetallic compounds in conformity with Eqns. (6) and (7) is quantitative.

In a study of the reaction of triethylgermane with triethylbismuth, Kruglaya et al. [42] established that, depending on the relative proportions of the starting materials, method B can be used to obtain not only $[(C_2H_5)_3Ge]_3Bi$ but also products of the partial replacement of ethyl by triethylgermyl groups:

$$n\,(C_2H_5)_3GeH + (C_2H_5)_3Bi \longrightarrow n\,C_2H_6 + [(C_2H_5)_3Ge]_nBi\,(C_2H_5)_{3-n},$$

where n = 1–3.

Method B has not yet been further developed on these lines. Nevertheless, this method has certain limitations. Thus compounds containing Sn–Cd, Sn–Tl, Sn–Zn [41], and Sn–Hg [24,25] bonds cannot be obtained in this way. It may merely be supposed that compounds of this type are intermediates in the reaction of $(C_2H_5)_3SnH$ with ethyl derivatives of cadmium, thallium, zinc, and mercury, since ethane and hexaethyldistannane are formed in high yield in all these cases, e.g. [24,25]

$$2\,(C_2H_5)_3SnH + (C_2H_5)_2Hg \longrightarrow 2C_2H_6 + [(C_2H_5)_3Sn]_2Hg \downarrow (C_2H_5)_6Sn_2 + Hg$$

Method B has not yet been widely used with success for the synthesis of substances containing M–M′ groupings, where M and M′ are elements of the silicon subgroup. However, there are grounds for assuming[49] that this limitation can be overcome:

$$(C_6H_5)_3GeH + (C_4H_9)_3SnN(C_2H_5)_2 \longrightarrow (C_2H_5)_2NH + (C_4H_9)_3SnGe(C_6H_5)_3.$$

In spite of the above disadvantages, this is undoubtedly a general method. In particular, method B can be used to obtain organodielementary compounds containing an ionic bond between the inorganic elements as well as those in which the bond is covalent. The metallation of organogermanium hydrides by organolithium compounds in tetrahydrofuran medium is well known[2,12,50]. In some cases, e.g. in the reaction of triphenylgermane with butyl-lithium, the yield is quantitative:

$$(C_6H_5)_3GeH + C_4H_9Li \longrightarrow C_4H_{10} + (C_6H_5)_3GeLi. \quad (9)$$

Discussing this reaction, Gilman[50] indicates, not without justification, that it is analogous to corresponding reactions of diphenylphosphine and of triphenylmethane[51,52]:

$$(C_6H_5)_2PH + C_4H_9Li \longrightarrow C_4H_{10} + (C_6H_5)_2PLi^{51,53},$$
$$(C_6H_5)_3CH + C_4H_9Li \longrightarrow C_4H_{10} + (C_6H_5)_3CLi^{53,54}.$$

Compounds containing Sn–Li[55], As–Li[56], P–Mg[57], and Sb–Li[58] ionic bonds have been prepared in a similar manner.

Recently, after a series of unsuccessful attempts[50], $(C_6H_5)_3GeMgCl$ has been prepared by the reaction of triphenylgermane with allylmagnesium chloride in tetrahydrofuran[59]. Finally, reports have recently appeared of the use of method B for the synthesis of compounds containing Ge–P [54], Sn–P [60], and Sn–As[60] bonds:

$$(C_6H_5)_2PH + (C_2H_5)_3GeN(CH_3)_2 \longrightarrow (CH_3)_2NH + (C_2H_5)_3GeP(C_6H_5)_2,$$
$$(C_6H_5)_2MH + R_3SnN(CH_3)_2 \longrightarrow (CH_3)_2NH + R_3SnM(C_6H_5)_2,$$

where M = P, As and R = CH_3, C_2H_5.

Besides the general methods A and B, several less developed routes are known for the synthesis of organodielementary compounds of the type under discussion. Thus triethyltriethylsilylgermane was obtained in 1963, for example, by the action of sodium on a mixture of bromotriethylsilane and bromotriethylgermane in the absence of solvents[61]; symmetrical products, containing Si–Si and Ge–Ge bonds, are formed at the same time.

Wiberg et al. [15], in an endeavour to use the Wurtz reaction to obtain compounds containing an Si–Si bond, studied the action of liquid sodium amalgam on halogenotrimethylsilanes. This led them to the synthesis of bistrimethylsilylmercury:

$$2(CH_3)_3SiX + 2Na + Hg \rightarrow [(CH_3)_3Si]_2Hg + 2NaX,$$

where X = Cl, Br. The compounds $Hg[Si(CH_3)_3 - {}_nH_n]_2$, where n = 1, 2, could not be obtained by the action of sodium amalgam on methylbromosilanes, but there is no doubt that they are formed as intermediates in this process.

Several original methods were developed during 1963–1964 for the preparation of compounds containing Pb–S [62], Sn–Se[63,64], Sn–Te[63,64], Sn–S–Pb[65], Sn–S [63,66], Ge–S [67], and Si–Sb[68] bonds.

Organodimetallic and organopolymetallic compounds having covalent bonds between transition metals and metals of Group IV*b* have been investigated intensively during recent years. The possibility of preparing compounds of this type was first reported by Hein and his coworkers[69]: by the action of organolead hydroxides on $Ca[HFe(CO)_4]_2$ they obtained two types of compounds containing a covalent Pb–Fe bond – $[Alk_2PbFe(CO)_4]_2$ and $(R_3Pb)_2Fe(CO)_4$, where R represents phenyl or cyclohexyl.

A method based on the reactions of salts of hydrocarbonyls with organometallic halides of Group IV*b*, e.g.[70]

$$R_{4-n}SnCl_n + n\,Na[Co(CO)_4] \longrightarrow n\,NaCl + R_{4-n}Sn[Co(CO)_4]_n,$$

where n = 1,2 and R = CH_3, C_4H_9, proved to be more generally applicable. The compounds $(C_4H_9)_2SnFe(CO)_4$,[70] $[(C_6H_5)_2PbFe(CO)_4]_2$,[71] $C_5H_5Fe(CO)_2Si(CH_3)_3$,[72,73] $(C_6H_5)_3GeMn(CO)_5$,[74] and $(C_6H_5)_3GeFe(CO)_2C_5H_5$ [74] have been obtained in this way. Gorsich[75] used the same method to synthesise compounds containing covalent Sn–Mn, Pb–Mn, and Sn–Fe bonds.

In recent years two further methods have been worked out for the preparation of compounds containing an Sn–Fe bond. Compounds of the type $[R_2SnFe(CO)_4]_2$, where R = = CH_3, C_4H_9, have been obtained in low yields by the interaction of pentacarbonyliron and $R_2Sn(C_6H_5)_2$ in boiling ethylcyclohexane[76]. The second method is based on the reaction[77]

$$[C_5H_5Fe(CO)_2]_2 + SnCl_2 \longrightarrow [C_5H_5Fe(CO)_2]_2SnCl_2 \xrightarrow{+2C_2H_5MgBr} [C_5H_5Fe(CO)_2]_2Sn(C_2H_5)_2. \quad (A)$$

The compound A has also been synthesised by the reaction

$$2C_5H_5Fe(CO)_2Na + Cl_2Sn(C_2H_5)_2 \longrightarrow 2NaCl + A.$$

In 1964 Nesmeyanov and his coworkers prepared organodimetallic compounds containing Re–M, Mo–M, and W–M bonds, where M = Sn, Pb, by the reaction of organometallic chlorides with $NaRe(CO)_5$,[78] $NaMo(CO)_3C_5H_5$, $NaW(CO)_3C_5H_5$, and $NaCr(CO)_3C_5H_5$.[79]

Quite recently these workers[80] have obtained new polymetallic compounds of tin with carbonyls of metals in Groups VI–VIII by the reactions

$$(CO)_5MnSn(C_6H_5)_2Cl + NaM(CO)_n \longrightarrow (CO)_5MnSn(C_6H_5)_2M(CO)_n, \quad (M=Co, Re)$$
$$(CO)_5MnSn(C_6H_5)_2Cl + NaM'(CO)_3C_5H_5 \longrightarrow (CO)_5MnSn(C_6H_5)_2M'(CO)_3C_5H_5. \quad (M'=Mo, W)$$

The elaboration of methods for the synthesis of the above compounds has been accompanied by an investigation of their structure and reactivity. As early as 1957 it was suggested[70] that the tin and cobalt atoms in the compound $(C_4H_9)_2Sn[Co(CO)_3P(C_6H_5)_3]_2$ were linked indirectly through carbonyl groups. The view was also expressed[72,75] that the metal atoms were joined by a covalent bond in these compounds. In 1964 Bryan[81] studied the crystal structure of $(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$, and found that the Sn, Mn, and P atoms are collinear and are linked covalently. X-Ray examination[79] of $C_5H_5(CO)_3Mo–Sn(C_6H_5)_3$ also confirms the presence of a σ-bond between molybdenum and tin atoms.

The reactivity of these compounds is determined by the nature of the atoms forming the metal–metal bond. Some of the compounds (e.g. those containing Sn–Co[70], Fe–Si[72], Fe–Sn[76], Pb–Mn[75], and Sn–Mn[75] bonds) tend to undergo oxidation, and are prepared in an atmosphere of nitrogen. In contrast, compounds containing Cr–M, Mo–M, and

W–M bonds, where M = Sn, Pb[79], and also Sn–Re, Pb–Re[78], are quite stable.

Chlorine, bromine, and hydrogen chloride do not cleave Sn–Mn[75] and Sn–Re[78] bonds. They do cleave an Sn–C bond[75,78,79]:

$$(C_6H_5)_3SnMn(CO)_5 + 3Cl_2 \longrightarrow Cl_3SnMn(CO)_5 + 3C_6H_5Cl,$$
$$(C_6H_5)_3SnRe(CO)_5 + 2Br_2 \longrightarrow (C_6H_5)Br_2SnRe(CO)_5 + 2C_6H_5Br,$$
$$(C_6H_5)_3SnMo(CO)_3C_5H_5 + 2HCl \longrightarrow (C_6H_5)Cl_2SnMo(CO)_3C_5H_5 + 2C_6H_6.$$

Hydrogen chloride has a similar effect on $(C_6H_5)_3SnW(CO)_3(C_5H_5)$, $(C_6H_5)_2Sn[Mo(CO)_3C_5H_5]_2$, $(C_6H_5)_2Sn[W(CO)_3C_5H_5]_2$, and $(C_6H_5)_3SnFe(CO)_2C_5H_5$.[77,79]

According to Gorsich[75] pentacarbonyltriphenylstannylmanganese, like simple metal carbonyls[3], reacts with triphenylphosphine and triphenylarsine, a molecule of carbon monoxide being displaced. The resulting product (B) has been prepared also by an alternative synthesis:

$$\begin{array}{l} (C_6H_5)_3SnMn(CO)_5 + P(C_6H_5)_3 \xrightarrow{-CO} \\ \qquad\qquad\qquad\qquad\qquad\qquad (C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3 \quad (B) \\ (C_6H_5)_3SnCl + NaMn(CO)_4P(C_6H_5)_3 \xrightarrow{-NaCl} \end{array}$$

On treatment with chlorine in dichloromethane, compound (B) is converted into $Cl_3SnMn(CO)_4P(C_6H_5)_3$ in 64% yield.

III. PROPERTIES OF COMPOUNDS OF THE TYPE $(R_3M)_nM'$ (M = Si AND ITS ANALOGUES; M' = Hg, Cd, Sb, etc.)

Organodielementary compounds of the type $(R_3M)_nM'$ are very reactive and have very varied chemical properties. Unfortunately their structural analogues $(R_3C)_nM'$ have in general been little studied, and therefore it is impossible to make a precise comparison of the properties and reactivities of these two classes of compounds. Most of the chemical reactions which these compounds undergo involve cleavage of covalent M–M' bonds with preservation of the R_3M fragments.

1. Thermal and Photochemical Decomposition

In most compounds of the type $(R_3M)_nM'$ extraordinary reactivity is combined with great thermal stability. In the absence of atmospheric oxygen, tristriethylsilylantimony and all its isologues other than tristriethylstannylbismuth can be distilled in a vacuum without appreciable decomposition[44]. This property is possessed also by bistrimethylsilylmercury[15], bistriethylsilylmercury[24], and bistriethylgermylmercury[39]. The examples of $(C_2H_5)_3SiHgC_2H_5$, $(C_2H_5)_3SiSi(C_2H_5)_2HgC_2H_5$, $(C_2H_5)_3SiHgGe(C_2H_5)_3$, and $(C_2H_5)_3SiSi(C_2H_5)_2HgGe(C_2H_5)_3$ show that compounds containing Si–Hg–C, Si–Si–Hg–C, Si–Hg–Ge, and Si–Si–Hg–Ge groupings are more stable than the usual unsymmetrical organomercury compounds[24,25]. In spite of the complexity of their structure, they distil in a vacuum without decomposition or symmetrisation.

The thermal stability of compounds of the type $[(C_2H_5)_3M]_3M'$ is determined by the stability of the M–M' bonds, and diminishes in the sequence Si–Sb ≃ Ge–Sb > Si–Bi ≃ Ge–Bi > Sn–Sb > Sn–Bi > Ge–Tl [44]. The least stable compounds of this series break down according to the equation

$$2[(C_2H_5)_3M]_3M' \rightarrow 3(C_2H_5)_6M_2 + 2M', \quad (10)$$

where M = Ge, M' = Tl and M = Sn, M' = Bi; and of the $[(C_2H_5)_3M]_2M'$ series according to the equation

$$[(C_2H_5)_3M]_2M' \rightarrow (C_2H_5)_6M_2 + M', \quad (11)$$

where M = Si, Ge and M' = Cd. Bistrimethylsilylmercury decomposes in the same way[15].

Tristriethylsilylantimony decomposes at ~300° with the quantitative liberation of antimony and the formation of $(C_2H_5)_3Si^{\bullet}$ radicals. The latter abstract hydrogen from surrounding molecules, giving triethylsilane and a complicated mixture of high-boiling organosilicon compounds.

According to Eaborn and his coworkers[82] the decomposition of bistrimethylsilylmercury in solvents also goes by a free-radical mechanism. The trimethylsilyl radicals can dimerise, abstract hydrogen from toluene and other solvents, replace the methyl group in anisole, and undergo other elementary reactions.

The thermal breakdown of compounds of general formula $[(C_2H_5)_3M]_nM'$ usually involves, independently of its mechanism, quantitative separation of the metal M' in the free state[40,44]. The element M, on the other hand, remains combined even when $(C_2H_5)_3M$ fragments are subject to free-radical attack. Tristriethylstannylantimony is an exception, decomposing with partial separation of tin[44]. In the presence of 2–3 wt.% of $AlBr_3$ the decomposition of tristriethylstannylantimony and its bismuth analogue follows a quite different path, the reaction conforming exactly to the equation

$$4[(C_2H_5)_3Sn]_3M' \rightarrow 9(C_2H_5)_4Sn + 3Sn + 4M', \quad (12)$$

where M' = Sb, Bi. Compounds of the type of $AlCl_3$ have a similar effect on the mechanism of the thermal decomposition of hexaethyldistannane[83].

According to Wiberg the thermal breakdown of polymeric dimethylsilylenemercury, obtained by the action of sodium amalgam on dimethyldibromosilane[15], is accompanied by the separation of the free metal and the formation of Si–Si bonds:

$$[(CH_3)_2SiHg]_n \rightarrow n\,Hg + [(CH_3)_2Si]_n.$$

Organosilicon and organogermanium compounds of mercury have proved very sensitive to the action of light, which has enabled Neumann[46,47] to use ultraviolet radiation to decompose a polymer containing a $[Ge–Hg]_n$ chain — see Eqn. (3).

Razuvaev and his coworkers have shown[39] that bistriethylgermylmercury, while possessing quite high thermal stability, readily undergoes photolysis

$$[(C_2H_5)_3Ge]_2 \cdot Hg \xrightarrow{h\nu} (C_2H_5)_6Ge_2 + Hg,$$

even if the ultraviolet radiation is filtered through molybdenum glass.

This process probably does not involve the formation of kinetically independent $(C_2H_5)_3Ge$ radicals, since, when it is conducted in cumene, tetraethyltin, or t-butyl peroxide, these compounds act as inert solvents. This hypothesis is consistent also with the fact that the photolysis of triethylgermyltriethylsilylmercury does not result in the formation of compounds containing Si–Si and Ge–Ge bonds, as

might have been expected if $(C_2H_5)_3Ge^{\bullet}$ and $(C_2H_5)_3Si^{\bullet}$ radicals had escaped "from the cage" into the bulk of the solution [25]:

$$(C_2H_5)_3GeHgSi(C_2H_5)_3 \xrightarrow{h\nu} Hg + (C_2H_5)_3GeSi(C_2H_5)_3.$$

All the above information on the decomposition of organodielementary compounds has been obtained in work with pure substances in the absence of atmospheric oxygen. The literature also contains data on the breakdown of several unstable organodielementary compounds in the course of their synthesis. In considering these results it must be borne in mind that the mechanism of the decomposition may be very different in the presence of foreign substances — cf. Eqns. (10) and (12).

Wiberg et al. [15], investigating the possibility of synthesising compounds of type $[Si(CH_3)_nH_{3-n}]_2Hg$ (n = 1, 2) by the action of sodium amalgam on methylbromosilanes, found that they break down in two ways in the process of preparation — (a) with the formation of disilanes $[Si(CH_3)_nH_{3-n}]_2$ by a reaction analogous to (11) and (b) with the formation of compounds $(CH_3)_nSiH_{4-n}$ and $(CH_3)_nSiH_{2-n}$ by the disproportionation of silicon-containing groups split off from the mercury.

When n = 3 reaction takes place solely by the first route, and when n = 1 solely by the second. When n = 2 both types of decomposition occur at the same time, but disproportionation processes predominate. These workers also studied the interaction of mercury dichloride with triphenylsilylpotassium in liquid ammonia, and showed that the bistriphenylsilylmercury formed decomposes to a considerable extent during the synthesis:

$$[(C_6H_5)_3Si]_2Hg \xrightarrow{a} (C_6H_5)_6Si_2 + Hg$$
$$[(C_6H_5)_3Si]_2Hg \xrightarrow{b} Hg + (C_6H_5)_4Si + (C_6H_5)_2Si$$

Route (b), which represents a side-reaction in the decomposition of bistriphenylsilylmercury, is the main reaction in the thermolysis of bistriphenylsilylzinc and bistriphenylsilylbarium [15]. The diphenylsilene $(C_6H_5)_2Si$ which is thus formed is converted into phenylated polysilanes $(C_6H_5)_3Si[Si(C_6H_5)_2]_nSi(C_6H_5)_3$.

2. Reactions with Atmospheric Oxygen and with Peroxides

Compounds of the type $(R_3M)_nM'$ are readily oxidised, and react vigorously with organic peroxides. The reactions occur at room temperature with the evolution of heat. The oxidation of bistriethylgermylmercury [39,45] is accurately represented by the equation

$$2[(C_2H_5)_3Ge]_2Hg + O_2 \longrightarrow 2[(C_2H_5)_3Ge]_2O + 2Hg.$$

The reaction can be employed for the determination of mercury in a substance. Bistriphenylgermylmercury [45], bistriethylgermylcadmium [40], and bistriethylsilylmercury [24] are oxidised in a similar manner.

According to results obtained by Vyazankin et al. [24] the oxidation of ethyltriethylsilylmercury is preceded by its symmetrisation. As a result, the oxidation products are found to contain diethylmercury, metallic mercury, and hexaethyldisiloxane:

$$2(C_2H_5)_3SiHgC_2H_5 \longrightarrow (C_2H_5)_2Hg + [(C_2H_5)_3Si]_2Hg$$
$$+{}^1/_2O_2 \searrow$$
$$Hg + [(C_2H_5)_3Si]_2O$$

The reactions with acyl peroxides are represented by equally simple stoichiometric equations [24,39,44]:

$$[(C_2H_5)_3M]_2Hg + (C_6H_5COO)_2 \longrightarrow Hg + 2(C_2H_5)_3MOCOC_6H_5, \quad (13)$$

where M = Ge, Si; and

$$2[(C_2H_5)_3M]_3M' + 3(C_6H_5COO)_2 \longrightarrow 2M' + 6(C_2H_5)_3MOCOC_6H_5, \quad (14)$$

where M = Si, Ge, Sn and M′ = Sb, Bi.

Bistriethylgermylmercury reacts with dicyclohexyl peroxodicarbonate in a similar fashion, with a quantitative yield of mercury [25]:

$$[(C_2H_5)_3Ge]_2Hg + (C_6H_{11}OCOO)_2 \rightarrow Hg + 2(C_2H_5)_3GeOCOOC_6H_{11}.$$

The second product is unstable, and is readily decarboxylated with the formation of cyclohexyloxytriethylgermane.

When bistriethylgermylcadmium [40], its silicon analogue [43], and compounds containing Ge–Zn bonds [41] are treated with benzoyl peroxide, cadmium (zinc) benzoate is formed as well as $C_6H_5COOM(C_2H_5)_3$ (M = Ge, Si). Reduction of the central atom to the elementary state — cf. Eqns. (13) and (14) — does not take place. The reaction of tristriethylgermylthallium with benzoyl peroxide is represented by the equation

$$[(C_2H_5)_3Ge]_3Tl + 2(C_6H_5COO)_2 \rightarrow 3(C_2H_5)_3GeOCOC_6H_5 + TlOCOC_6H_5.$$

In the authors' opinion the reactions with acyl peroxides take place by a latent-radical mechanism with the intermediate formation of cyclic active complexes. This is consistent with the following facts:

1. The reactions of acyl peroxides with organodielementary compounds are exothermic. At 5–10° they are complete within a few minutes. Under these conditions the starting materials are severally stable, and do not initiate free-radical processes.

2. Free-radical reactions are usually complicated. They involve the formation of multicomponent mixtures, which does not occur in the present cases.

3. Dibromoethane (see below) reacts similarly to acyl peroxides with organodielementary compounds. Reactions with monobromo-derivatives, in which the formation of cyclic active complexes is improbable, take place only under the influence of heat or light.

The ability of organodielementary compounds to react with acyl peroxides under mild conditions is not a specific property of substances containing M–M′–M groupings: benzoyl peroxide reacts equally vigorously with ethyltriethylsilylmercury, which contains a single Si–Hg bond [24]. Finally, the earlier papers of Razuvaev, Vyazankin, and their collaborators showed that acyl peroxides react at ~ 20° with hexaethyldistannane [83–85], diethyltin [37] (the polymeric nature of which has recently been rigorously proved [86]), and also with substances containing branched chains of tin atoms [85,87], by smoothly cleaving the Sn–Sn bonds. Polymeric diphenyltin reacts with benzoyl peroxide with the partial rupture of Sn–Sn bonds [88].

The Si–Si bond in hexaethyldisilane, on the other hand, is not cleaved by acyl peroxides even under conditions such that the latter break down, when the reaction aquires a free-radical character [83] and shows great complexity.

In contrast to acyl peroxides, t-butyl peroxide does not react with organodielementary compounds at room temperature. Moreover, as has been stated above, under mild conditions it is possible to accomplish the photodecomposition of bistriethylgermylmercury without affecting the t-butyl peroxide [24]. This is probably the first case

of a homolytic process in which a peroxy-compound acts as an inert solvent.

3. Reactions with Halogenated Derivatives

The photochemical reactions of halogeno-derivatives with ordinary organometallic compounds containing a single metal atom have been investigated in detail and discussed by Razuvaev and his coworkers [89-91]. The reactions usually occur by a free-radical mechanism:

$$R_nM \xrightarrow{h\nu} R_{n-1}M^{\cdot} + R^{\cdot},$$
$$R_{n-1}M^{\cdot} + R'X \longrightarrow R_{n-1}MX + R',$$

where R and R′ are aliphatic or aromatic groups, M is an n-valent metal, and X = Cl, Br, more rarely I. The fate of the radicals R and R′ which are formed is determined by their structure, also by the nature of the halogeno-derivative R′X, and by the properties of the initial organometallic compound R_nM.

The photochemical reactions of alkyl halides with organodielementary compounds follow a quite different scheme, e.g. [24,39]

$$[(C_2H_5)_3Ge]_2Hg + 2RBr \xrightarrow{h\nu} 2(C_2H_5)_3GeBr + R_2Hg,$$

where R = C_2H_5, C_6H_5, $C_6H_5CH_2$, 1-$C_{10}H_7$. The authors assume these reactions to occur "in a cage" with homolytic cleavage of C–Br and Ge–Hg bonds. Alkyl bromides react in a similar way with compounds of type $[(C_2H_5)_3M]_3Sb$ on heating [44]:

$$[(C_2H_5)_3M]_3Sb + 3RBr \longrightarrow 3(C_2H_5)_3MBr + R_3Sb,$$

where M = Sn, Ge; R = $C_6H_5CH_2$, cyclo-C_5H_9. The yields of the compounds R_3Sb vary from 57% to 75%. Finally, the reaction of bistriethylsilylcadmium with ethyl bromide (~80° for 2 h) yields bromotriethylsilane (36%) and diethylcadmium (76%). [43] Under comparable conditions bistriethylgermylcadmium [40] reacts with alkyl bromides by a different, more usual route:

$$[(C_2H_5)_3Ge]_2Cd + 2RBr \rightarrow CdBr_2 + 2(C_2H_5)_3GeR,$$

where R = C_2H_5, $C_6H_5CH_2$.

Bisdibutylstibylmagnesium reacts similarly with allyl bromide, the products being allyldibutylantimony (31%) and magnesium bromide [68]. The reaction of ethyl bromide with compounds containing Ge–Zn bonds also proceeds "normally", with the formation of $ZnBr_2$ and $R_3GeC_2H_5$. [41]

A very characteristic reaction of organodielementary compounds containing M–M′–M groupings is that with 1,2-dibromoethane, which is exothermic and is complete at room temperature within a few minutes, e.g. [42]

$$[(C_2H_5)_3Ge]_2Hg + CH_2BrCH_2Br \rightarrow 2(C_2H_5)_3GeBr + Hg + C_2H_4.$$

The yields of mercury, ethylene, and bromotriethylgermane are respectively 97%, 75%, and 58%. Tristriethylsilylantimony reacts similarly with excess of dibromoethane [44]. With equimolecular proportions of the reactants, ethylene and bromotriethylsilane are formed together with a viscous, coloured, readily oxidisable substance, which is regarded as polymeric triethylsilylantimony:

$$n[(C_2H_5)_3Si]_3Sb + n\,CH_2BrCH_2Br \rightarrow n\,C_2H_4 + 2n(C_2H_5)_3SiBr + [(C_2H_5)_3SiSb]_n.$$

This hypothesis is consistent with the reactions of $(cyclo\text{-}C_6H_{11})_2SbLi$ [58] and $C_6H_5AsLi_2$ [92] with dibromoethane, in the course of which Sb–Sb and As–As bonds are formed. The products are tetracyclohexyldistibine and arsenobenzene, together with ethylene and lithium bromide.

The reaction of dibromoethane with bistriethylgermylcadmium [40] differs somewhat from those considered above. In this case the central atom (cadmium) is not reduced to the free metal. The reaction products are cadmium bromide (74%), ethylene (73%), and bromotriethylgermane (86%). In the reaction between dibromoethane and tristriethylgermylthallium the thallium passes from the tervalent to the univalent state:

$$[(C_2H_5)_3Ge]_3Tl + 2CH_2BrCH_2Br \rightarrow 2C_2H_4 + 3(C_2H_5)_3GeBr + TlBr.$$

4. Reactions with Metals and Their Salts

The reactions with metals of ordinary organometallic compounds (containing a single metal atom), accompanied by the transfer of radicals from one metal to the other, have been investigated in detail and are widely employed for synthetic purposes. The first attempt to transfer a trimethylsilyl radical from metal to metal (from mercury to zinc and aluminium) was undertaken by Wiberg et al. [15] They showed that, when bistrimethylsilylmercury reacts with zinc, which occurs only at high temperatures, the mercury is not replaced by zinc but dimethylmercury is formed. The mechanism of the process was not discussed. Reaction of bistrimethylsilylmercury with activated aluminium takes place at a more moderate temperature (80°) with the quantitative separation of mercury and a mixture of products containing no Si–Al bonds.

In the authors' opinion this is explained by the instability of the $>Al\text{–}Si(CH_3)_3$ groups in the tristrimethylsilylaluminium formed as intermediate:

$$[(CH_3)_3Si]_3Al \rightarrow Al(CH_3)_3 + 3(CH_3)_3Si.$$

This is followed by "saturation" of the dimethylsilene by the $(CH_3)_3Si$ groups of the bistrimethylsilylmercury, with the production of polysilanes of the $(CH_3)_3Si[Si(CH_3)_2]_nSi.(CH_3)_3$ series. In an investigation of the same problem Vyazankin et al. [93] showed that at 50° metallic mercury displaces cadmium from diethylcadmium, bistriethylsilylcadmium, and its germanium analogue:

$$Hg + R_3Cd \rightarrow Cd + R_2Hg,$$

where R = C_2H_5, $(C_2H_5)_3Si$, $(C_2H_5)_3Ge$.

Mercury reacts more vigorously (within 1½ h at 20°) with tristriethylgermylthallium, the yield of bistriethylgermylmercury reaching 78%. The resulting mercury compound can in turn act as starting material for the synthesis of triethylgermyl-lithium and its sodium analogue in high yields:

$$[(C_2H_5)_3Ge]_2Hg + 2M \rightarrow Hg + (C_2H_5)_3GeM,$$

where M = Li, Na. The reaction goes readily in tetrahydrofuran medium.

Organodielementary compounds acts as reducing agents towards metal salts. Wiberg et al. found [15] that bistriphenylsilylbarium and bistriphenylsilylzinc reduce silver nitrate to metallic silver. Similar behaviour is shown by the compound containing Al–Si bonds obtained by the action of triphenylsilylpotassium on aluminium chloride in tetrahydrofuran.

According to Razuvaev and his coworkers [93] bistriethylgermylcadmium reacts with mercuric chloride to form mercury (71%), cadmium chloride (82%), and chlorotriethylgermane (31%), the reaction being exothermic. Metallic mercury is formed also by the interaction of mercuric chloride with compounds containing Ge–Zn–Ge groups [41].

5. Other Reactions

The interaction of organodielementary compounds with acids involves cleavage of the M–M′–M grouping, the central atom separating as the free metal, e.g. [42]

$$2\,[(C_2H_5)_3Ge]_3Bi + 3\,CH_3COOH \rightarrow 3\,(C_2H_5)_3GeOCOCH_3 + 3\,(C_2H_5)_3GeH + 2\,Bi,$$

Acetic acid reacts similarly with bistriethylgermylmercury [42] and with bistriethylgermylcadmium [93]. Bistrimethylsilylmercury reacts with hydrochloric acid [15] in the same way; the reaction is quantitative, and may serve as a method of analysis for mercury.

Under normal conditions bistriethylgermylmercury and its silicon analogue are stable to hydrolysis or alcoholysis even after many months of contact with water or alcohols. Bistriethylgermylcadmium [40,93], on the other hand, interacts with these reagents under mild conditions:

$$[(C_2H_5)_3Ge]_2Cd + RH \longrightarrow (C_2H_5)_3GeH + (C_2H_5)_3GeR + Cd,$$

where R = OH, n-C_3H_7O.

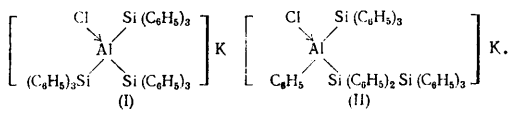
The hydrolysis of bistriphenylbarium with moist methanol proceeds differently [15]:

$$[(C_6H_5)_3Si]_2Ba + 4H_2O \longrightarrow Ba(OH)_2 + 2H_2 + 2\,(C_6H_5)_3SiOH.$$

In the authors' opinion the complex $KCl.Al[Si(C_6H_5)_3]_3$, which is the first organodielementary compound containing covalent Si–Al bonds, is hydrolysed by alcoholic potassium hydroxide in a similar manner. The fact that this involves the evolution of only two moles of hydrogen, not the three that might have been expected from the equation

$$KCl\cdot Al[Si(C_6H_5)_3]_3 + 6H_2O \longrightarrow KCl + Al(OH)_3 + 3\,(C_6H_5)_3SiOH + 3H_2,$$

led the authors to assign to the complex the structure (II) instead of (I)



(I) (II)

For the reaction of this substance with hydrochloric acid see Ref. 15.

Zinc hydroxide and triphenylsilane have been isolated from the hydrolysis of bistriphenylsilylzinc with dilute hydrochloric acid [15]. Compounds of the type $(C_2H_5)_3GeZn.[Ge(C_2H_5)_2]_nGe(C_2H_5)_3$, which are formed by the interaction of triethylgermane and diethylzinc, are hydrolysed in a similar manner [41].

IV. PROPERTIES OF COMPOUNDS OF TYPE $R_3M–M′R_3$ (WHERE M AND M′ ARE ELEMENTS OF GROUP IV*b*)

In comparison with the compounds described in the preceding Section, those of the $R_3M–M′R_3$ series, where M and M′ represent elements of the silicon subgroup, possess immeasurably smaller reactivity. The completely arylated compounds $(C_6H_5)_3SiGe(C_2H_5)_3$, [8] $(C_6H_5)_3SiSn(C_6H_5)_3$, [94] and $(C_6H_5)_3GeSn(C_6H_5)_3$ [17] are closely similar in chemical properties to hexaphenyldisilane and its analogues, and differ sharply from hexaphenylethane in the absence of any tendency to dissociate into radicals. These compounds are stable to atmospheric oxygen, and are not cleaved by water, alcohols, or acids. In the fully phenylated compounds the Si–Ge bond is not ruptured by iodine in boiling chloroform or by organolithium compounds, whereas the Ge–Sn bond is unstable towards these reagents. According to Gilman and his coworkers, replacement of phenyl by alkyl groups in compounds of this type leads to a strengthening of the M–M′ bonds.

Metals of the lithium subgroup and their alloys are extremely effective agents for the cleavage of M–M′ bonds. Correct choice of solvent is extremely important for the successful conduct of the reactions. Triphenyltriphenylsilylgermane is cleaved by a sodium–potassium alloy in ether [8]. In the case of triphenyltriphenylstannylgermane this alloy is effective only in tetrahydrofuran [17]. Trimethyltriphenylsilyltin is split by sodium in liquid ammonia [95]. Triphenyltriethylsilylgermane is cleaved at the Si–Ge bond by lithium in triethylamine [10]. Aliphatic derivatives containing Si–Ge [61] and Si–Sn [15] bonds have recently been synthesised, but very little work has been done on their chemical properties. It has been established that stannylsilanes of the types $R_3SnSiR'_3$ and $(R_3Sn)_2SiR'_2$ (where R = C_2H_5, C_4H_9, C_6H_5, and R′ = CH_3, C_6H_5) are stable in air. They undergo an exothermic reaction with $TiCl_4$, reducing it to $TiCl_3$. The latter can be isolated from the mixture in a polymerisation-active state [15].

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This review makes it plain that three types of organodielementary compounds containing covalent M–M′ bonds exist. Compounds in which M and M′ are elements of the silicon subgroup belong to the least varied type. Representatives of this group are the least reactive. Substances containing M–M′–M groups (M = Si and its analogues and M′ = Hg, Cd, Al, Bi, etc.), on the other hand, are highly reactive, and their properties are extremely unusual.

The third type of compounds, which has been studied intensively, contains metal–transition metal bonds. The striking features of compounds of this type are their variety and the unexpected stability of the M–M′ groupings.

All the compounds which have been described are of great interest for study of the nature of the chemical bond in general and of the metal–metal bond in particular. As research develops, they will undoubtedly also find practical application.

1. D.Wittenberg and H.Gilman, Quart.Rev., 13, 116 (1959).
2. R.K.Ingham, S.D.Rosenberg, H.Gilman, and F.Rijkens, "Organotin and Organogermanium Compounds" (Translated into Russian), Inostr.Lit., Moscow, 1962.
3. H.Zeiss (Editor), "Organometallic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1964.
4. F.Rijkens and G.J.M.van der Kerk, "Organogermanium Chemistry", Utrecht, 1964.
5. L.C.Willemsens, "Organolead Chemistry", New York, 1964.
6. H.Gilman and T.C.Wu, J.Org.Chem., 18, 753 (1953).
7. J.G.Milligan and C.A.Kraus, J.Amer.Chem.Soc., 72, 5297 (1950).
8. H.Gilman and C.W.Gerow, J.Amer.Chem.Soc., 78, 5823 (1956).
9. H.Gilman and C.W.Gerow, J.Amer.Chem.Soc., 77, 4675 (1955).
10. C.A.Kraus and W.K.Nelson, J.Amer.Chem.Soc., 56, 195 (1934).
11. H.Gilman and C.W.Gerow, J.Amer.Chem.Soc., 77, 5509 (1955).
12. R.J.Cross and F.Glockling, J.Chem.Soc., 4125 (1964).
13. H.Gilman and S.D.Rosenberg, J.Amer.Chem.Soc., 74, 531 (1952).

14. C.Tamborski, F.E.Ford, and E.J.Soloski, J.Org.Chem., 28, 181 (1963).
15. E.Wiberg, O.Stecher, H.J.Andraschek, L.Kreuzbichler, and E.Staude, Angew.Chem., 75, 516 (1963).
16. H.Gilman and S.D.Rosenberg, J.Org.Chem., 18, 680 (1953).
17. H.Gilman and C.W.Gerow, J.Org.Chem., 22, 334 (1957).
18. L.C.Willemsens and G.J.M.van der Kerk, J.Organometallic Chem., 2, 260 (1964).
19. W.Drenth, M.J.Janssen, and G.J.M.van der Kerk, J.Organometallic Chem., 2, 265 (1964).
20. W.Drenth, L.C.Willemsens, and G.J.M.van der Kerk, J. Organometallic Chem., 2, 279 (1964).
21. W.Drenth, M.J.Janssen, G.J.M.van der Kerk, and J.A.Vliegenthart, J.Organometallic Chem., 2, 205 (1964).
22. D.Blake, G.E.Coates, and J.M.Tate, J.Chem.Soc., 618 (1961).
23. M.V.George, G.D.Lichtenwalter, and H.Gilman, J.Amer. Chem.Soc., 81, 978 (1959).
24. N.S.Vyazankin, G.A.Razuvaev, and E.N.Gladyshev, Dokl. Akad.Nauk SSSR, 155, 830 (1964).
25. N.S.Vyazankin, G.A.Razuvaev, E.N.Gladyshev, and T.G.Gurikova, Dokl.Akad.Nauk SSSR, 155, 1108 (1964).
26. H.Schumann and M.Schmidt, Angew.Chem., 76, 344 (1964).
27. K.Jones and M.F.Lappert, Proc.Chem.Soc., 22 (1964).
28. I.G.M.Campbell, G.W.A.Fowles, and L.A.Nixon, J.Chem. Soc., 3026 (1964).
29. H.C.Clark and R.J.O'Brien, Proc.Chem.Soc., 2583 (1963).
30. M.V.George, B.J.Gaj, and H.Gilman, J.Org.Chem., 24, 624 (1959).
31. M.V.George and H.Gilman, J.Amer.Chem.Soc., 81, 3288 (1959).
32. H.Schumann, H.Köpf, and M.Schmidt, Angew.Chem., 76, 607 (1964).
33. H.Schumann, H.Köpf, and M.Schmidt, Chem.Ber., 97, 2395 (1964).
34. I.G.M.Campbell, G.W.A.Fowles, and L.A.Nixon, J.Chem. Soc., 1389 (1964).
35. R.S.Dickson and B.O.West, Austral.J.Chem., 14, 555 (1961).
36. H.Nöth and K.H.Hermannsdörfer, Angew.Chem., 76, 377 (1964).
37. N.S.Vyazankin, G.A.Razuvaev, and S.P.Korneva, Zhur. Obshch.Khim., 33, 1046 (1963).
38. N.S.Vyazankin, G.A.Razuvaev, and S.P.Korneva, Zhur. Obshch.Khim., 34, 2787 (1964).
39. N.S.Vyazankin, G.A.Razuvaev, and E.N.Gladyshev, Dokl. Akad.Nauk SSSR, 151, 1326 (1963).
40. N.S.Vyazankin, G.A.Razuvaev, and V.T.Bychkov, Dokl. Akad.Nauk SSSR, 158, 382 (1964).
41. N.S.Vyazankin, G.A.Razuvaev, S.P.Korneva, O.A.Kruglaya, and R.F.Galiulina, Dokl.Akad.Nauk SSSR, 158, 884 (1964).
42. O.A.Kruglaya, N.S.Vyazankin, and G.A.Razuvaev, Zhur. Obshch.Khim., 35, 394 (1965).
43. N.S.Vyazankin, G.A.Razuvaev, and V.T.Bychkov, Zhur. Obshch.Khim., 35, 395 (1965).
44. N.S.Vyazankin, O.A.Kruglaya, G.A.Razuvaev, and G.S.Semchikova, Dokl.Akad.Nauk SSSR, 166, 99 (1966).
45. K.Kühlein, Diplomarbeit, Universität Giessen, 1963.
46. W.P.Neumann, Angew.Chem., 75, 679 (1963).
47. W.P.Neumann and K.Kühlein, Annalen, 683, 1 (1965).
48. M.Pang and E.J.Becker, J.Org.Chem., 29, 1948 (1964).
49. R.Sommer, W.P.Neumann, and B.Schneider, Tetrahedron Letters, 3875 (1964).
50. H.Gilman and C.W.Gerow, J.Amer.Chem.Soc., 78, 5435 (1956).
51. K.Issleib and A.Tzschach, Chem.Ber., 92, 1118 (1959).
52. G.W.Parshall and R.V.Lindsey, J.Amer.Chem.Soc., 81, 6273 (1959).
53. H.Gilman and R.V.Young, J.Org.Chem., 1, 315 (1936).
54. J.Satge, M.Lesbre, and M.Baudet, Compt.rend., 259, 4733 (1964).
55. G.Wittig, F.Meger, and G.Lange, Annalen, 571, 167 (1951).
56. A.Tzschach and G.Pacholke, Chem.Ber., 97, 419 (1964).
57. K.Issleib and H.J.Deyling, Chem.Ber., 97, 946 (1964).
58. K.Issleib and B.Hamann, Z.anorg.Chem., 332, 179 (1964).
59. H.Gilman and E.A.Zuech, J.Org.Chem., 26, 3035 (1961).
60. K.Jones and M.F.Lappert, J.Organometallic Chem., 3, 295 (1965).
61. J.M.Shackelford, H.De Schmertzing, C.H.Heuther, and H.Podall, J.Org.Chem., 28, 1700 (1963).
62. A.W.Krebs and M.C.Henry, J.Org.Chem., 28, 1911 (1963).
63. H.Schumann, K.F.Thom, and M.Schmidt, Angew.Chem., 75, 138 (1963).
64. H.Schumann, K.F.Thom, and M.Schmidt, J.Organometallic Chem., 2, 361 (1964).
65. H.Schumann, K.F.Thom, and M.Schmidt, J.Organometallic Chem., 1, 167 (1963).
66. H.Schumann, K.F.Thom, and M.Schmidt, J.Organometallic Chem., 2, 97 (1964).
67. J.Ruidisch and M.Schmidt, Chem.Ber., 96, 1424 (1963).
68. S.Herbstmann, J.Org.Chem., 29, 986 (1964).
69. F.Hein, H.Pobloth, and E.Heuser, Z.anorg.Chem., 248, 84 (1941); 249, 293 (1942); 254, 138 (1947); 255, 125 (1948).
70. W.Hieber and R.Breu, Chem.Ber., 90, 1270 (1957).
71. F.Hein, P.Kleinert, and W.Jehn, Naturwiss., 44, 34 (1957).
72. T.S.Piper, D.Lemal, and G.Wilkinson, Naturwiss., 43, 129 (1956).
73. W.Hieber and C.Scharfenberg, Ber., 73, 1012 (1940).
74. D.Seyferth, H.P.Hofmann, R.Burton, and J.F.Helling, Inorg.Chem., 1, 227 (1962).
75. R.D.Gorsich, J.Amer.Chem.Soc., 84, 2486 (1962).
76. R.B.King and F.G.A.Stone, J.Amer.Chem.Soc., 82, 3833 (1960).
77. F.Bonati and G.Wilkinson, J.Chem.Soc., 179 (1964).
78. A.N.Nesmeyanov, K.N.Anisimov, N.E.Kolobova, and V.N.Khondozhko, Dokl.Akad.Nauk SSSR, 156, 383 (1964).
79. A.N.Nesmeyanov, K.N.Anisimov, N.E.Kolobova, and M.Ya.Zakharova, Dokl.Akad.Nauk SSSR, 156, 612 (1964).
80. A.N.Nesmeyanov, K.N.Anisimov, N.E.Kolobova, and M.Ya.Zakharova, Izv.Akad.Nauk SSSR, Ser.Khim., 1122 (1965).
81. R.F.Bryan, Proc.Chem.Soc., 232 (1964).
82. A.G.Beaumont, C.Eaborn, R.A.Jackson, and R.W.Walsingham, J.Organometallic Chem., 5, 297 (1966).
83. N.S.Vyazankin, G.A.Razuvaev, and O.A.Kruglaya, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 2008 (1962).
84. G.A.Razuvaev, N.S.Vyazankin, and O.A.Shchepetkova, Zhur.Obshch.Khim., 30, 2498 (1960).
85. G.A.Razuvaev, N.S.Vyazankin, and O.A.Shchepetkova, Tetrahedron, 18, 667 (1962).
86. W.P.Neumann and J.Pedain, Annalen, 672, 34 (1964).
87. G.A.Razuvaev, O.A.Shchepetkova, and N.S.Vyazankin, Zhur.Obshch.Khim., 31, 1401 (1961).
88. H.Kuivila and E.Jakusik, J.Org.Chem., 26, 1430 (1961).
89. G.A.Razuvaev, N.S.Vyazankin, Yu.I.Dergunov, and E.N.Gladyshev, Izv.Akad.Nauk SSSR, Ser.Khim., 849 (1964).
90. A.Schönberg, "Präparative organische Photochemie" (Translated into Russian), Inostr.Lit., Moscow, 1963, p.348.
91. O.A.Reutov, "Teoreticheskie Problemy Organicheskoi Khimii" (Theoretical Problems of Organic Chemistry), Izd. Moskov.Gos.Univ., 1956.
92. D.A.Thornton, J.S.African Chem.Inst., 17, 71 (1964).
93. N.S.Vyazankin, G.A.Razuvaev, and V.T.Bychkov, Izv. Akad.Nauk SSSR, Ser.Khim., 1665 (1965).

94. T.C.Wu, Iowa State Coll.J.Sci., 27, 282 (1953).
95. C.A.Kraus and H.Eatough, J.Amer.Chem.Soc., 55, 5008 (1933).

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STEREOCHEMISTRY OF ORGANIC COMPOUNDS OF PHOSPHORUS AND ARSENIC

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I. INTRODUCTION

Acquaintance with the world's chemical literature must lead to the conclusion that interest has grown appreciably during recent years in problems of the stereochemistry not only of carbon compounds but also of those of other elements — nitrogen, phosphorus, sulphur, arsenic, antimony, etc. — in the Periodic System. The reason for the increasing number of stereochemical investigations is undoubtedly that this field, which until not long ago was regarded as one of the most abstract, is beginning to acquire ever increasing practical importance. Stereochemical features of structure have a great influence on the biochemical properties of organic compounds. Knowledge of the configurational relationships among various types of optically active compounds is of practical and theoretical importance. It is required in many fields of biochemistry for the study of metabolism and the action of drugs, in working out theoretical problems of biogenesis, etc. The use of optically active reactants often considerably facilitates study of the mechanism of chemical reactions. A systematic study of the stereochemistry of reactions will inevitably lead in the future to a more profound understanding of the chemical changes occurring in living Nature.

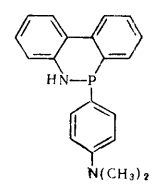
Interest has grown considerably during recent years in the stereochemistry of organic compounds of phosphorus and arsenic, especially the former. The first attempts to obtain optically active compounds containing asymmetric phosphorus and arsenic atoms were made at the beginning of the present century. In 1911 Meisenheimer[1,2] showed for the first time, with ethylmethylphenylphosphine oxide as example, that phosphorus can act as an asymmetric centre in a molecule. The first optically active organic compound of arsenic — the dextrorotatory benzylmethyl-1-naphthylphenylarsonium iodide — was obtained in 1921 by Burrows and Turner[3].

A. Michaelis, J. Meisenheimer, A. E. Arbuzov, B. A. Arbuzov, G. Kh. Kamai, D. M. Coyne, H. S. Aaron, L. Horner, J. Michalski, and many others have devoted their researches to the difficult but interesting field of the stereochemistry of organophosphorus and organoarsenic compounds, and definite progress has now been achieved.

II. STEREOCHEMISTRY OF ORGANIC COMPOUNDS OF TERVALENT PHOSPHORUS AND ARSENIC

The phosphorus atom has the electronic configuration $(1s^2)(2s^2)(2p^6)(3s^2)(3p^3)$, so that it can have covalencies of 3–6 in its compounds. Organic derivatives of tervalent phosphorus can be regarded as derivatives of phosphine PH_3 in which one, two, or three hydrogen atoms have been replaced by organic radicals. Phosphines have the configuration of a trigonal pyramid. This is evident from the fact that in the tervalent state phosphorus utilises only $3p$-electrons, as is confirmed by the valency angle of 94° in phosphine and 101 ± 3° in trimethylphosphine. Thus a tertiary phosphine $PR^1R^2R^3$ should exist in the form of two optical isomers, related to one another as an object to its mirror image. Until recently derivatives of tervalent phosphorus remained almost uninvestigated from the point of view of optical isomerism. The calculated frequency of oscillation of the phosphorus atom[4] is 5×10^6 s^{-1}. Calculations by Weston[5] showed on the basis of the oscillation frequency that the half-life (or rate of racemisation) for trimethylphosphine is 2 h at 7°. It appeared that optical isomers of asymmetric tertiary phosphines would be stable only at low temperatures. Until recently investigators adhered to this view, and in fact no-one attempted to resolve tertiary phosphines of the type $PR^1R^2R^3$ into optical isomers.

It was suggested that the stability of optical isomers of tervalent phosphorus compounds should be increased if the phosphorus atom formed part of a ring system, since oscillation of the phosphorus atom would then be impeded. Campbell and Way[6] have resolved the cyclic phosphine 10-*p*-dimethylaminophenyl-9,10-dihydro-9-aza-10-phosphaphenanthrene



into optical isomers by reducing the optically active isomeric oxides of this phosphine with lithium tetrahydroaluminate. The isolated isomers of the phosphine proved to have far greater optical stability than could have been expected from Weston's calculations[5]. The dextrorotatory isomer, which has an initial rotation of $[\alpha]_D^{21} = 141°$, acquires a rotation of 114° after 5 h; the corresponding specific rotation of the laevorotatory isomer changed from -128° to -97° in 4 h. It was discovered that the decrease in the angle of rotation was due not to racemisation