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Reactions of Organic Derivatives of the Elements with Polyhalogenomethanes

S.F.Zhil'tsov and O.N.Druzhkov

The review discusses the reactivity of organic derivatives of the elements (with one or two "non-organic" atoms) in relation to halogenomethanes. The chemical reactivity of true organic derivatives of elements in Groups I-V in reactions with alkyl halides is determined by the type of the compound and the nature of the element-carbon bond. Particular attention has been devoted to initiated processes.
The bibliography includes 250 references.

CONTENTS

I. Introduction	126
II. Reactions of organometallic compounds of Group I elements	126
III. Reactions of organometallic compounds of Group II elements	127
IV. Reactions of organic compounds of Group III elements	131
V. Reactions of organic compounds of Group IV elements	132
VI. Reactions of two-element organic compounds	135
VII. Reactions of organic compounds of Group V elements	136

I. INTRODUCTION

Extensive empirical data have now accumulated on reactions of organic derivatives of the elements (ODE) with polyhalogeno-derivatives of methane. These reactions are of definite theoretical interest and are employed in organic syntheses.

The reactivity of ODE depends on the type of compound and the nature of the element and the organic group bound to the atom of the element. Some ODE react with polyhalogenomethanes at a low temperature and others only on heating, irradiation with ultraviolet light, or in the presence of initiators. The sharp differences between the reactivities of ODE and the use of different conditions in studies on the reactions are frequently the reasons for the contradictory interpretation of the mechanism of the reaction of ODE with polyhalogenomethane.

The literature dealing with the reactions of true organic compounds of Group I–V elements with polyhalogenomethanes is critically examined in this review in order to be able to discuss the mechanisms of these processes, their general characteristics, and the general relations governing them.

II. REACTIONS OF ORGANOMETALLIC COMPOUNDS OF GROUP I ELEMENTS

The reactions of organometallic metallic compounds (OMC) of Group I elements with polyhalogenomethanes have been investigated in greatest detail for lithium derivatives. Organolithium compounds react vigorously with di-, tri-, and tetra-halogenomethanes in hydrocarbon, ether, or tetrahydrofuran (THF) solutions at a low temperature (between −100° and −60°C). The greatest number of communications deal with reactions of compounds of the type RLi (R = CH_3,[1-6] iso-C_3H_7,[1,7] n-C_4H_9,[8-12] s-C_4H_9, t-C_4H_9, n-C_5H_{11},[2] cyclo-C_6H_{11},[10] C_6H_5,[13,14] and substituted vinyl[15,16]) with methylene dichloride. The main products of the reaction are lithium chloride and saturated and unsaturated cyclopropane hydrocarbons and their chloro-derivatives.

It has been shown[12] that dichloromethyl-lithium is formed as an intermediate:

$$RLi + CH_2Cl_2 \rightarrow RH + CCl_2HLi\ .$$

The presence of a dichloromethyl derivative in the reaction mixture was confirmed by reactions with mercury(II) chloride and zinc chloride, which led to the isolation of bis(dichloromethyl)mercury (m.p. 154–155°C) in almost quantitative yield and bis(dichloromethyl)zinc, which is stable at room temperature.

Dichloromethyl-lithium is an unstable compound, which decomposes above −60°C. There is no unanimous view concerning the mechanism of its decomposition. Arguments are quoted in favour of a bimolecular decomposition[12]:

$$2Cl_2HCLi \rightarrow 2\ LiCl + ClCH{=}CHCl\ .$$

However, the majority of investigators postulate the participation of free chlorocarbene in reactions of organolithium compounds with methylene dichloride:

$$Cl_2CHLi \rightarrow LiCl + \ddot{C}HCl,$$

which makes it possible to account for the presence in the reaction mixture of many of the compounds formed.

Insertion or addition reactions are most characteristic of carbenes and a number of monographs[17,18] and reviews[19-21] have been devoted to them.

The reaction of organolithium compounds with methylene dichloride in the presence of olefins[4-6,9,22] leads to the formation of chlorocyclopropanes in high yields:



This reaction may be employed for preparative purposes. Chlorocarbene reacts with benzene, phenol[23], pyrrole, and indole[24] with ring expansion and adds to triphenylphosphine[25] with formation of ylide.

Chlorocarbene is inserted in the C–Li bond of the initial organometallic derivative with formation of a substituted chloromethyl-lithium derivative[10,14]:

$$R{-}Li + \ddot{C}HCl \rightarrow RCHClLi .$$

The decomposition of the latter gives rise to alkyl- or aryl-carbenes:

$$RCHClLi \rightarrow LiCl + R\ddot{C}H$$

(R = alkyl[8,10] or aryl[13,14]).

Alkylcarbenes tend to undergo intermolecular isomerisation, which leads to the formation of olefins and cyclopropanes. Thus the reaction of pentyl-lithium with methylene dichloride in ethyl ether solution at −30°C or in pentane solution at 30°C results in the formation of hex-1-ene (94–95%)† and n-propylcyclopropane (5–6%) owing to the isomerisation of the pentylcarbene formed initially. The principal products isolated in the analogous reactions of s-butyl-lithium and t-butyl-lithium are 2-methylbut-1-ene, ethylcyclopropane and *trans*-dimethylcyclopropane for the first compound and 2-methylbut-1-ene, 2-methylbut-2-ene, and 1,1-dimethylcyclopropane for the second[10].

In contrast to alkylcarbenes, arylcarbenes[13,14] undergo telomerisation or recombine to form symmetrical diarylethylenes (30–34%).

In the reaction of organolithium compounds with methylene dibromide, a bromine atom and not a hydrogen atom is split off from the latter:

$$RLi + CH_2Br_2 \rightarrow RBr + CH_2BrLi \rightarrow \ddot{C}H_2 + LiBr .$$

The carbene adds to olefins[4,26,27] or is inserted in the carbon–metal bond of the organometallic compound taken in excess[28]. Bromobenzene (25%), benzyl bromide (21%), and dibenzyl (37%) were isolated from the reaction mixture of phenyl-lithium[29] with methylene dibromide. In the reaction of methyl-lithium[30] with methylene dibromide the products are methyl bromide (5%), ethyl bromide (48%), and propyl bromide (13%):

$$RLi + \ddot{C}H_2 \rightarrow RCH_2Li ,$$

$$RCH_2Li + \ddot{C}H_2 \rightarrow RCH_2CH_2Li ,$$

$$RCH_2Li\ (RCH_2CH_2Li) + CH_2Br_2 \rightarrow RCH_2Br\ (RCH_2CH_2Br) + CH_2BrLi ,$$

$$RCH_2Li + RCH_2Br \rightarrow RCH_2CH_2R + LiBr .$$

Butyl-lithium reacts with bromochloromethane[31] at −110°C with formation of chloromethyl-lithium (90%) and bromochloromethyl-lithium (10%). The first compound was identified by carboxylation to chloroacetic acid. Its reaction with cyclohexene gives norcarane[32]. Chloromethyl-lithium is less stable than dichloromethyl-lithium.

Reactions of organolithium compounds with substituted dihalogenomethanes (dibromodiphenylmethane[33], 1,1-dibromoalkanes[30,34,35], and dichlorodiphenylmethane[29]) have been described. The products of the reaction of phenyl-lithium with dichlorodiphenylmethane are tetraphenylethylene and triphenylmethane.

Organolithium compounds react vigorously with tri- and tetra-halogenomethanes. The primary reaction product is a trihalogenomethyl derivative of lithium:

$$RLi + CXCl_3 \rightarrow RX + Cl_3CLi ,$$

$$(R{=}CH_3,\ C_2H_5,\ n\text{-}C_4H_9,\ C_6H_5\ \text{etc.},\ X{=}H,\ Cl,\ Br,\ I) .$$

† Here and henceforth the yield of the reaction product is indicated in brackets.

The formation of trichloromethyl-lithium has been demonstrated in the reaction of butyl-lithium with chloroform in tetrahydrofuran[39] or in a tetrahydrofuran–ethyl ether–petroleum ether mixture[11] at −110°C. The compound was identified by the products of its reaction with mercury(II) chloride, carbon dioxide, and benzophenone. The reaction with mercury(II) chloride led to the isolation of bis(trichloromethyl)mercury (m.p. 146.5–148.5°C with decomposition) in 91% yield. It has been noted[36] that trichloromethyl-lithium is less stable than dichloromethyl-lithium. At −65°C it decomposes in 30 min to the extent of 40–50%:

$$Cl_3CLi \rightarrow LiCl + \ddot{C}Cl_2 .$$

Tribromomethyl-lithium was obtained by the reaction[37] of butyl-lithium or phenyl-lithium with carbon tetrabromide in tetrahydrofuran solution at −110°C and also by the reaction[38] of trichloromethyl-lithium with carbon tetrabromide. It was identified by carboxylation to tribromoacetic acid. Bromoform is formed in its reaction with methanol[37].

Organolithium compounds react with $CXCl_3$ (X = H, Cl, Br, or I) in the presence of cyclohexene[11,25,26,36,39,40] with formation of 7,7-dichloronorcarane, the yield of which is 50–90%. However, the yield of 7,7-dibromonorcarane in the analogous reaction with bromoform[4,27] and carbon tetrabromide[26,37] is low (8–19%).

The formation of dihalogenonorcaranes has been regarded[33,36,41–43] as a result of the predominantly molecular interaction of trihalogenomethyl-lithium with the olefin and not the addition of the free dihalogenocarbene to cyclohexene.

Franzen[44–46] believes that butyl-lithium reacts with dibromodifluoromethane, forming free difluorocarbene. The latter adds to olefins, triphenylphosphine, and butyl-lithium taken in excess. The involvement of difluorocarbene is postulated in the reactions of the lithium compound with trifluoroiodomethane[47], which takes place with formation of tetrafluoroethylene (43%).

The reactions of organolithium compounds with polyhalogenomethanes are frequently employed as a source of carbenes for a wide variety of organic syntheses based on the latter.

Thus alkyl and aryl derivatives of lithium react vigorously with polyhalogenomethanes at a low temperature. In the initial stages of the reaction the corresponding halogenomethyl derivatives of lithium are produced. They decompose with formation of lithium halides and reactive carbenes.

It is to be expected that the organometallic compounds of the remaining alkali metals will react similarly with polyhalogenomethanes.

III. REACTIONS OF ORGANOMETALLIC COMPOUNDS OF GROUP II ELEMENTS

The reactions of organometallic compounds of Group II elements with polyhalogenomethanes have been investigated for magnesium, zinc, cadmium, and mercury compounds. In such reactions the organic derivatives of these elements show markedly different reactivities.

Organomagnesium compounds react vigorously with various halogeno-derivatives at low temperatures and therefore their reactions do not require initiation.

The alkyl compounds of zinc and cadmium react fairly readily with halogenomethanes ($CHBr_3$, $CHCl_3$, CCl_4) but the reactions of aryl derivatives take place only in the presence of an initiator.

The reactions of organomercury compounds with polyhalogenomethanes are observed on heating to the temperature of the onset of decomposition of the former compounds. The reactions occur more readily in the presence of oxygen and peroxides or under the influence of ultraviolet light.

1. Reactions of Organomagnesium, Organozinc, and Organocadmium Compounds

The reactions of organomagnesium compounds with polyhalogenomethanes have been investigated for asymmetric compounds of the type RMgX (R = alkyl, or aryl and X = halogen). The reaction of phenylmagnesium bromide[48] with chloroform leads to the formation of triphenylmethane (80%). Its yield is lower (about 25%) in the corresponding reactions[49] with bromoform and iodoform. Later it was shown[50] that chloroform reacts with phenylmagnesium bromide to form triphenylmethane (76%) and small amounts of biphenyl and bromobenzene. The products of the reaction of bromoform and iodoform with this magnesium derivative are tetraphenylethane (up to 60%) and triphenylmethane[51]. The products of the reaction of phenylmagnesium bromide with carbon tetrachloride are hexaphenylethane (50–80%) and bromobenzene[52]. A complex mixture of products is formed in the reactions of alkyl derivatives of magnesium. Ethylmagnesium bromide reacts with carbon tetrachloride to form methane and ethylene[53]. The products of its reaction with bromoform are ethyl bromide, methylene dibromide, 3-methylpentane, and acetylene[51].

The reactions of organomagnesium compounds have been investigated in greatest detail by Villieras[54–57]. It was established that these reactions, like those of organolithium compounds, lead to the formation of intermediate halogenomethyl derivatives of the metal. In the reaction of isopropylmagnesium chloride with dihalogenomethane[56] at −80°C the exchange of the halogen in CH_2X_2 for the MgCl group is observed, the halogens being arranged in the following sequence in terms of the ease of their exchange:

$$I > Br \gg Cl,$$
$$RMgCl + CH_2X_2 \rightarrow RX + XCH_2MgCl.$$

Grignard reagents react with bromotrichloromethane[56], carbon tetrachloride, and chloroform[57], forming the trichloromethyl derivative CCl_3MgX. The final products of the reaction of RCH_2MgCl with chloroform are RCH_2Cl and a mixture of olefins ($RCH{=}CHCH_3R$ and $RCH{=}CH_2$). In the reaction of organomagnesium compounds[57] with bromoform the products are alkyl bromides and the dibromomethyl compound $CHBr_2MgX$, which decomposes with formation of bromocarbene or reacts with the initial organometallic compound:

$$CHBr_2MgX + RMgX \rightarrow MgXBr + \underset{\downarrow}{RCHBrMgX}$$
$$R\ddot{C}H + MgXBr.$$

The alkylcarbene is converted into a mixture of various olefins. It is suggested[57] that the reactions of organomagnesium compounds with polyhalogenomethanes proceed via a four-centre transition state:

$$CHBr_3 + RMgCl \rightleftharpoons \left[\begin{array}{c} HBr_2C \cdots MgCl \\ \vdots \quad \vdots \\ Br \cdots R \end{array}\right] \rightleftharpoons CHBr_2MgCl + RBr.$$

Organozinc and organocadmium compounds R_2M exhibit the same reactivity in relation to polyhalogenomethanes, which depends on the nature of the group R linked to the metal atom. Alkyl compounds of zinc[58–60] and cadmium[61] react vigorously with bromoform, chloroform, and carbon tetrachloride at room temperature. Diethylzinc also reacts with chloroiodomethane[62] and methylene di-iodide[63,64] with formation of unsaturated hydrocarbons. The reaction of diethylzinc with methylene di-iodide[65,66] and also with ethylidene di-iodide[67,68] in the presence of olefins is accompanied by the formation of cyclopropanes (30–90%):

$$(C_2H_5)_2Zn + CH_2I_2 \rightarrow C_2H_5I + C_2H_5ZnCH_2I \xrightarrow{>C=C<} \underset{CH_3}{>C(-C<)-C<} + C_2H_5ZnI.$$

Aryl compounds (diphenylzinc and diphenylcadmium[69]) do not react with chloroform and carbon tetrachloride even when the reaction mixture is heated to 100°C. However, in the presence of oxygen the reactions proceed readily at room temperature.

The principal products of the reaction of diethylcadmium with carbon tetrachloride are ethyl chloride, ethylcadmium chloride, and cadmium chloride, the yield of the latter increasing with the molar ratio[61] $CCl_4 : R_2Cd$. When cyclohexene is introduced into the reaction mixture, the reaction is retarded so much that an increase of temperature to 80°C is required for its occurrence. 7,7-Dichloronorcarane was not detected in the products. The mechanism of the reaction of diethylcadmium with carbon tetrachloride is somewhat obscure.

As mentioned above, aryl compounds of zinc and cadmium are inert with respect to polyhalogenomethanes under the usual conditions. When oxygen is introduced into the reaction mixture[70,71], the reaction between phenyl derivatives [of the two metals] and $CXCl_3$ (X = H or Cl) proceeds readily with formation of benzene (X = H), chlorobenzene (X = Cl), ααα-trichlorotoluene, phenol, biphenyl, and hexachloroethane. The initiating effect of oxygen is associated with the oxidation of the organometallic compound, which is accompanied by the generation of phenyl radicals. The latter react with the polyhalogenomethane or the initial zinc or cadmium compound:

$$C_6H_5^{\cdot} + CXCl_3 \rightarrow C_6H_5X + Cl_3C^{\cdot},$$
$$(X{=}H, D, Cl)$$
$$C_6H_5^{\cdot}(Cl_3C^{\cdot}) + (C_6H_5)_2M \rightarrow C_6H_5C_6H_5\,(C_6H_5CCl_3) + C_6H_5M^{\cdot},$$
$$(M{=}Zn, Cd)$$
$$C_6H_5M^{\cdot} + CXCl_3 \rightarrow C_6H_5MCl + \dot{C}XCl_2,$$
$$2\dot{C}XCl_2 \rightarrow CXCl_2{-}CXCl_2.$$

Thus the reaction of diphenylzinc[71] and diphenylcadmium[70] with chloroform and carbon tetrachloride in an oxygen atmosphere involves the participation of free radicals.

2. Reactions of Organomercury Compounds

The greatest number of communications deal with reactions of organomercury compounds with chloroform and carbon tetrachloride. Mercury compounds react with polyhalogenomethanes on heating to the temperatures of the onset of decomposition of the organometallic compound. As early as 1864, Alexeyeff and Beilstein concluded[60] that the reaction of diethylmercury with bromoform is accompanied by the formation of ethyl bromide and propene. In the reaction of diethylmercury with iodoform[72], ethylmercury iodide, ethyl iodide, ethylene, and acetylene are formed. Diphenylmercury does not react at 130°C with bromoform and chloroform but does react with iodoform, forming tri-iodomethylphenylmercury[73] $C_6H_5HgCI_3$ (m.p. 153–155°C). We believe that the asymmetric mercury

compound and the corresponding halogenomethyl derivatives of magnesium discussed above are not formed by the same mechanism. In the present case the reaction probably begins with the decomposition of iodoform:

$$CHI_3 \rightarrow HI + \ddot{C}I_2 ,$$
$$(C_6H_5)_2Hg + HI \rightarrow C_6H_6 + C_6H_5HgI ,$$
$$C_6H_5HgI + \ddot{C}I_2 \rightarrow C_6H_5HgCI_3 ,$$
$$C_6H_5HgCI_3 + \ddot{C}I_2 \rightarrow C_6H_5HgI + C_2I_4 .$$

These processes account for the formation of the reaction products.

Diphenylmercury and dinaphthylmercury [74-76] begin to react with chloroform and carbon tetrachloride above 200°C. The principal products of the reaction of diphenylmercury with the above halogenomethanes are phenylmercury chloride, benzene, $\alpha\alpha\alpha$-trichlorotoluene, and hexachloroethane. The reaction has a free-radical mechanism:

$$R_2Hg \rightarrow RHg^{\cdot} + R^{\cdot} , \quad (1)$$
$$RHg^{\cdot} + CXCl_3 \rightarrow RHgCl + Cl_2XC^{\cdot} , \quad (2)$$
$$(X=H, Cl)$$
$$R^{\cdot} + CXCl_3 \rightarrow RX + Cl_3C^{\cdot} ,$$
$$Cl_3C^{\cdot} + R_2Hg \rightarrow RCCl_3 + RHg^{\cdot} , \quad (3)$$
$$2Cl_3C^{\cdot} \rightarrow C_2Cl_6 .$$

Phenylmercury radicals not only react with the polyhalogenomethane to form phenylmercury chloride but also decompose with the liberation of mercury or recombine:

$$2RHg^{\cdot} \rightarrow RHg{-}HgR \rightarrow R_2Hg + Hg .$$

Alkyl compounds of mercury [77-79] R_2Hg (R = C_2H_5, [79] n-C_3H_7, [78,80] iso-C_3H_7, [77] and n-C_4H_9 [79]) react in a more complex manner with chloroform and carbon tetrachloride, forming alkylmercury chloride, mercury, calomel, alkyl chloride, chloroform, saturated hydrocarbons (RH) and olefins (R-H), and hexachloroethane, and in the reaction with chloroform also methylene dichloride. The initial stage of these reactions is the dissociation of the organometallic compound into radicals according to Eqn. (1). Possibly there is a molecular interaction of the organomercury compound with the polyhalogenomethane accompanied by the formation of alkyl mercury chloride and free radicals:

$$R_2Hg + CXCl_3 \rightleftarrows [R_2Hg \cdot Cl_3XC] \rightarrow RHgCl + R^{\cdot} + Cl_2XC^{\cdot} . \quad (4)$$

One can also postulate that in the initial reaction stage a trichloromethyl derivative of mercury is formed and serves as a source of dichlorocarbene, which would initiate the process. However, the introduction into the reaction mixture of trichloromethyl compounds of mercury [79], which decompose under the reaction conditions with generation of $\ddot{C}Cl_2$, did not lead to its acceleration.

The occurrence of free-radical processes has been confirmed using inhibitors [79]. It has been shown [77-79] that initiated decomposition of the initial organometallic compound plays a considerable role in these reactions:

$$R^{\cdot} (Cl_2XC^{\cdot}) + RHgR \rightarrow RH (Cl_2XCH) + \dot{R}_{-H}HgR . \quad (5)$$

This results in the formation of unstable organomercury radicals with an unpaired electron at the carbon atom. The nature of their decomposition depends to a considerable degree on the nature of the alkyl group linked to the metal atom:

$$\dot{R}_{-H}HgR \rightarrow R_{-H} + RHg^{\cdot} , \quad (a)$$
$$\dot{R}_{-H}HgR \rightarrow R_{-H} + Hg + R^{\cdot} . \quad (b) \quad (6)$$

The radicals formed from the ethyl derivative decompose both via mechanism (6a) and (6b). With increase of the chain length of the primary alkyl residue (R = n-C_3H_7 and n-C_4H_9), their decomposition takes place predominantly via reaction (6b), while the corresponding derivative containing a secondary alkyl residue (iso-C_3H_7 and s-C_4H_9) is cleaved with formation of alkylmercury radicals via reaction (6a). The latter react with chloroform and carbon tetrachloride forming the alkyl mercury chloride [reaction (2)].

Alkyl radicals participating in the reaction initiate the decomposition of the organometallic compound or react with polyhalogenomethanes. It has been shown for isopropyl radicals [77] that they abstract from chloroform not only hydrogen atoms but also chlorine atoms. The ease of abstraction of hydrogen, deuterium, and chlorine from $CHCl_3$ and $CDCl_3$ decreases in the sequence H > Cl ≃ D.

Among organomercury compounds, alkoxy-derivatives [80,81] of the type RHgOR′ react with chloroform most readily. Their reaction [81] takes place at room temperature with a quantitative yield of the corresponding trichloromethyl compounds:

$$RHgOR' + CHCl_3 \rightarrow RHgCCl_3 + R'OH$$
$$(R=n\text{-}C_3H_7, \text{ cyclo-}C_6H_{11}, C_6H_5CH_2, C_6H_5; R'=(CH_3)_3C) .$$

Thus the thermal reactions of the symmetrical mercury compounds R_2Hg with polyhalogenomethanes have a free-radical mechanism.

Organomercury compounds dissociate into radicals under the influence of ultraviolet light:

$$R_2Hg \rightarrow 2R^{\cdot} + Hg ,$$
$$R_2Hg \rightarrow RHg^{\cdot} + R^{\cdot} .$$

The photochemical reaction of mercury compounds with polyhalogenomethanes takes place readily at room temperature. These processes were investigated in greatest detail by Razuvaev and coworkers.

The photolysis of R_2Hg has been investigated in solution in bromoform (R = C_6H_5, [82] carboxyphenyl, or methoxycarbonylphenyl [83]), chloroform (R = CH_3, [84] C_2H_5, [85] 2-methoxycarbonylethyl [86], mesityl [87], $C_6H_5CH_2$, [88] $C_6H_5CH_2CH_2$, [89] C_6H_5, [82,90] o-tolyl [91], p-tolyl [92], p-anisyl [93], p-chlorophenyl [91], carboxyphenyl and methoxycarbonylphenyl [83], α-naphthyl [94], and β-naphthyl [95]) and carbon tetrachloride (R = CH_3, [84,96] C_2H_5, [79] n-C_3H_7, [78,79] iso-C_3H_7, [78,79] n-C_4H_9, [79] s-C_4H_9, [79] $C_6H_5CH_2$, [96] C_6H_5, [75,90,96] o-tolyl [91], p-tolyl [92], p-anisyl [93], carboxyphenyl and methoxycarbonylphenyl [83], α-naphthyl [94], and β-naphthyl [95]). In these reactions the RHg radicals abstract a halogen atom from the polyhalogenomethane. Mercury and calomel are formed together with the alkyl- or aryl-mercury chloride. The yields of these substances depend on the nature of the group R linked to the mercury atom. The relative amounts of mercury and alkylmercury chloride vary particularly markedly in the photochemical reactions of alkyl derivatives of mercury with carbon tetrachloride. As in thermal reactions, the yield of mercury increases with the chain length of the primary alkyl residue [79] (more than 90% for di-n-propylmercury). On the other hand, with the secondary isopropyl residue, the corresponding alkylmercury chloride is formed preferentially. In these processes the organomercury compounds undergo initiated decomposition via mechanisms (5) and (6). In contrast to thermal reactions, the olefins formed react with the solvent giving 1,1,1-trichloroalkanes or 1,1,1,3-tetrachloroalkanes:

$$-\overset{|}{C}=\overset{|}{C}- + Cl_3C^{\cdot} \rightarrow -\overset{|}{\dot{C}}-\overset{|}{C}CCl_3 \xrightarrow{CXCl_3} -\overset{|}{C}X-\overset{|}{C}CCl_3 \quad (7)$$
$$(X = H, Cl)$$

The presence of calomel in the reaction mixture is due to the reaction of mercury[97] with carbon tetrachloride or the dealkylation of alkylmercury chloride under the influence of radicals:

$$RHgCl + Cl_3C^{\cdot} \rightarrow CHCl_3 + \dot{R}_{-H}HgCl \rightarrow R_{-H} + {}^1/_2Hg_2Cl_2 . \quad (8)$$

The radical R formed in the reaction interacts with the organometallic compound or the halogeno-derivative, abstracting chlorine from carbon tetrachloride or hydrogen from chloroform and bromoform, with the exception of benzyl radicals[88] which largely recombine. In the photolysis of organomercury compounds in a mixture of a protic solvent (alcohol, ethylcellosolve) and carbon tetrachloride the R radicals react only with the first solvent, abstracting a hydrogen atom[98] and forming RH.

In the photochemical reactions with chloroform and carbon tetrachloride the asymmetric organometallic compounds RHgR′ also undergo dealkylation[88,98,99] with formation of RHgCl. The more firmly bound group remains attached to mercury. In many cases the process is accompanied by symmetrisation[100]:

$$2RHgR' \rightarrow R_2Hg + R'_2Hg .$$

Among the mixed mercury compounds, peroxy-derivatives of the type[101] RHgOOR′, hydroxides[102-106] RHgOH (R = C_6H_5,[102,103,105,106] $C_6H_5CH_2$,[103] mesityl[104], or *p*-dimethylaminophenyl[104]), and benzyl- and phenylmercury derivatives of succinimide[107,108] react most readily with carbon tetrachloride and chloroform. The reactions of these compounds lead to the formation of the corresponding chlorides RHgCl.

In the case of many hydroxides, the initial stage of the process is usually believed to be their dissociation into radicals:

$$RHgOH \rightarrow RHg^{\cdot} + HO^{\cdot} .$$

We believe that the mechanism of the reaction of the hydroxides with polyhalogenomethanes is more complex. It is doubtful if these compounds undergo homolysis at the Hg–O bond, which is stronger than the Hg–C bond. Probably the comparatively ready occurrence of the reaction is due to the participation in it of oxides, which are present in the hydroxides and are formed as a result of the dehydration of the latter[109]:

$$2RHgOH \rightleftarrows (RHg)_2O + H_2O .$$

This conclusion is based on the finding that alkoxy-derivatives of mercury RHgOR′ (in this case R′ = RHg) react with polyhalogenomethanes under fairly mild conditions.

The reactions of organomercury compounds with halogenomethanes do not take place solely under the influence of heat and light. Organic peroxides and oxygen have an initiating effect on them. Razuvaev showed[74] that the temperature in the reaction of diphenylmercury with carbon tetrachloride may be considerably reduced (from 260° to 50°C) when benzoyl peroxide is introduced into the reaction mixture. Acetyl peroxide has a similar effect[110]. The principal reaction products are phenylmercury chloride, ααα-trichlorotoluene, and hexachloroethane. In the reaction with chloroform the products are benzene, phenylmercury chloride, and also small amounts of ααα-trichlorotoluene and hexachloroethane. The initial stage of the process is the decomposition of the acyl peroxide:

$$(R'COO)_2 \rightarrow R'^{\cdot} + R'COO^{\cdot} + CO_2 ,$$
$$(R' = CH_3, C_6H_5)$$

The methyl or phenyl radicals formed in this process interact with carbon tetrachloride generating trichloromethane radicals. ααα-Trichlorotoluene is formed via reaction (3) and phenylmercury chloride via reaction (2). The reaction of asymmetric organometallic compounds RHgR′ with carbon tetrachloride in the presence of peroxides[111,112] is similar to that of diphenylmercury. It has been established that the affinity for the free radical $Cl_3C^{\cdot}$ decreases in the series 2,4,6-$(CH_3)_3C_6H_2$, α-$C_{10}H_7$, *p*-$CH_3C_6H_4$, *o*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, C_6H_5, C_2H_5, C_4H_9, $C_6H_5CH_2$, cyclo-C_6H_{11}.

The more reactive group R in RHgR′ recombines with the trichloromethyl radical and the group R′ remains bound to mercury in the resulting compound R′HgCl.

Alkyl derivatives of mercury react somewhat differently with carbon tetrachloride in the presence of a peroxide. The principal products of the reaction of dibutylmercury[113] with carbon tetrachloride (100°C, 7h) initiated by benzoyl peroxide are 1,1,1,3-tetrachloropentane, butyl chloride, chloroform, mercury, and butylmercury chloride. 1,1,1-Trichloropentane was not detected. On the basis of the reaction products, it was concluded that trichloromethyl radicals react with the organometallic compound, forming chloroform:

$$Cl_3C^{\cdot} + R_2Hg \rightarrow \underset{\text{(olefin)}}{R_{-H}} + CHCl_3 + RHg^{\cdot} .$$

It is believed[113] that butylmercury radicals decompose with liberation of mercury (up to 63–73%) or react with carbon tetrachloride, forming butylmercury chloride. The formation of tetrachloropentane is due to reaction (7). Under the influence of radicals, dibutylmercury undergoes a decomposition in this reaction analogous to that described above for the thermal and photochemical reactions of alkyl compounds of mercury[79] [reactions (5) and (6)].

Perbenzoic acid[114], the peroxides formed by the oxidation of benzaldehyde or cyclohexene[115], t-butyl peroxide[116], t-butyl hydroperoxide[116], and oxygen[79] have an initiating effect on the reaction of diphenylmercury with carbon tetrachloride or chloroform. It is suggested that perbenzoic acid initially reacts with the organometallic compound to form phenylmercury perbenzoate[114], which decomposes into radicals. t-Butyl hydroperoxide reacts similarly[116]:

$$R_2Hg + (CH_3)_3COOH \rightarrow RH + RHgOOC(CH_3)_3 \begin{cases} \rightarrow RHg^{\cdot} + (CH_3)_3COO^{\cdot}, \\ \rightarrow RHgO^{\cdot} + (CH_3)_3CO^{\cdot} . \end{cases}$$

The initiating effect of t-butyl peroxide[78,116] is due to its reaction with the organometallic compound induced by the nucleophilic attack by active oxygen on the mercury atom with formation of a complex. The decomposition of the latter is accompanied by the generation of free radicals:

$$R_2Hg + (CH_3)_3COOC(CH_3)_3 \rightleftarrows \left[\begin{matrix} R\text{—}Hg\text{—}R \\ \uparrow \\ (CH_3)_3COOC(CH_3)_3 \end{matrix} \right] \rightarrow \begin{matrix} RHgOC(CH_3)_3 \\ + \\ R^{\cdot} + (CH_3)_3CO^{\cdot} \end{matrix}$$

(R = n-C_3H_7,[78] iso-C_3H_7,[78] or C_6H_5[116]).

In these reactions alkyl derivatives of mercury and the alkylmercury chlorides formed mainly decompose under the influence of radicals[78] [see reactions (5), (6), and (8)]. The olefins thus produced react with the solvent, giving a high yield of the corresponding trichloro- or tetrachloroalkanes [reaction (7)].

Organometallic compounds of the type R_2Hg (R = C_2H_5,[79] n-C_3H_7,[78] iso-C_3H_7,[117,118] n-C_4H_9,[79] s-C_4H_9,[79] t-C_4H_9,[118] cyclo-C_6H_{11},[119] or C_6H_5[79]) react comparatively readily with carbon tetrachloride or chloroform in the presence of oxygen. The initial step in the reaction is nucleophilic attack by oxygen on the mercury atom in the

organometallic compound accompanied by the formation of an unstable organomercury peroxide[118,120,121]:

$$R_2Hg + O_2 \rightleftarrows [R_2Hg^{\cdot}O_2] \rightarrow RHgOOR \begin{cases} \longrightarrow RHg^{\cdot} + RO_2^{\cdot}, \\ \longrightarrow RHgO^{\cdot} + RO^{\cdot}. \end{cases}$$

The oxidation products of an organomercury compound[118,120,121] are an alkoxy-compound RHgOR, an alcohol ROH, a ketone or an aldehyde, mercury, and also hydrocarbons. The oxidation is accompanied by the generation of free radicals which react with polyhalogenomethanes. The alkoxy-compound obtained also readily reacts with chloroform and carbon tetrachloride. This results in the formation of a trichloromethyl compound of mercury, which decomposes under the reaction conditions into an alkylmercury chloride and dichlorocarbene:

$$RHgCCl_3 \rightleftarrows RHgCl + \ddot{C}Cl_2 . \qquad (9)$$

In the reactions with added cyclohexene in the reaction mixture, 7,7-dichloronorcarane was detected[79]. Seyferth et al. established[122] that reaction (9) is reversible and the rate of decomposition depends on the nature of the solvent.

The oxidation of organomercury compounds in solution in polyhalogenomethanes is accompanied by initiated decomposition processes via mechanisms (5), (6), and (8), which in this case are less important than in thermal and photochemical reactions in the absence of oxygen[79]. Regardless of the nature of the alkyl group, the main dealkylation product of the organometallic compound is alkylmercury chloride.

Diphenylmercury is known to react[123] with chloroform in the presence of bismuth trichloride, forming phenylmercury chloride, benzene, and biphenyl. Bismuth trichloride probably behaves as a catalyst.

Thus organomercury compounds of the type R_2Hg do not react with polyhalogenomethanes under ordinary conditions. Their reaction is observed only under the influence of heat, ultraviolet light, oxygen, or organic peroxides and proceeds via a free-radical mechanism.

IV. REACTIONS OF ORGANIC COMPOUNDS OF GROUP III ELEMENTS

The reactions of organometallic compounds of group III elements with polyhalogenomethanes have been investigated mainly for alkyl compounds of aluminium and thallium. There is only one report[124] of the reaction of triethylindium-ether with chloroform and bromoform in hexane solution accompanied by the formation of the corresponding diethylindium halide. The reactions of organoboron compounds with polyhalogenomethanes have been described using as examples the reactions of vinylarylboron butoxide with bromotrichloromethane[125] at room temperature under the influence of ultraviolet light:

$$CH_2{=}CH{-}\underset{\displaystyle C_6H_5}{\underset{|}{B}}{-}OC_4H_9 + CBrCl_3 \rightarrow Cl_3CCH_2CHBr{-}\underset{\displaystyle C_6H_5}{\underset{|}{B}}{-}OC_4H_9 .$$

The first report on the reaction of organoaluminium compounds with chloroform and carbon tetrachloride was published by Hilpert and Grüttner[126]. In particular, they concluded that, when triphenylaluminium is dissolved in chloroform, triphenylmethane and a crystalline substance, probably diphenylaluminium chloride, are formed. The views concerning the reactivity of alkyl compounds of aluminium in relation to polyhalogenomethanes and the mechanism of their reaction with the latter are extremely contradictory.

It has been noted[127] that triethylaluminium reacts slowly with methylene dichloride at 55°C. Under these conditions, ethylaluminium sesquichloride and diethylaluminium hydride do not react with this chloro-derivative. However, methylene di-iodide reacts with triethylaluminium[128] (in molar proportions of 1 : 2) in benzene solution at room temperature with formation of ethyl iodide and ethylene. The iodomethyl derivative of diethylaluminium is formed as an intermediate:

$$R_3Al + CH_2I_2 \rightarrow RI + R_2AlCH_2I \rightarrow R_2AlI + {}^1/_2C_2H_4 .$$

When the reaction was carried out with added cyclohexene, norcarane was isolated (20%). The participation of free carbene in the reaction has not been suggested[129,130].

Chloroform reacts with triethylaluminium[127,131] more vigorously than does methylene dichloride. For equimolar proportions of the reactants, the main products are methylene dichloride and ethyl chloride. At 70°C hydrocarbons (butane, butene, hexane, and hexene) are formed in addition to the above compounds. The reaction of diethylaluminium hydride with chloroform (at the boiling point of the latter) is accompanied by the formation of methyl chloride. Under these conditions, ethylaluminium sesquichloride does not react with trichloromethane. The reaction of aluminium compounds with chloroform is regarded as a free-radical process[127]. However, Miller[128] believes that the reactions of organoaluminium compounds with trihalogenomethanes proceed via a stage involving the formation of halogenomethyl derivatives. In particular, he showed that triethylaluminium reacts with bromoform in benzene solution, forming the dibromomethyl derivative $(C_2H_5)_2AlCHBr_2$.

There are contradictory data on the behaviour of organoaluminium compounds in carbon tetrachloride solutions. According to some reports[132,133], a mixture of such compounds explodes. According to others[134,135], aluminium compounds do not react with carbon tetrachloride at room temperature and the latter is recommended as a solvent for them. Vigorous reaction between triethylaluminium and carbon tetrachloride with evolution of gaseous substances is observed in the presence of titanium tetrachloride[135]. It is suggested that diethylaluminium dichloride is formed initially and is then readily dealkylated[136] by carbon tetrachloride. It is believed[135] that the reaction proceeds with participation of a carbonium ion:

$$2CCl_4 + C_2H_5AlCl_2 \rightleftarrows 2Cl_3C^{\cdot} + C_2H_5^{+}AlCl_4^{-},$$

$$C_2H_5^{+}AlCl_4^{-} + CCl_4 \rightarrow C_2H_5Cl + CCl_3^{+}AlCl_4^{-} \rightarrow AlCl_3 + CCl_4 ,$$

$$C_2H_5^{+}AlCl_4^{-} + C_2H_5AlCl_2 \rightarrow C_2H_6 + (AlCl_4^{-} + \overset{+}{C}_2H_4AlCl_2) \downarrow 2\,AlCl_3 + C_2H_4 .$$

In contrast to ethylaluminium dichloride, diethylaluminium chloride does not react with carbon tetrachloride in boiling benzene[137].

Reinheckel[127,138,139] elucidated the reactions of organoaluminium compounds with carbon tetrachloride to the greatest extent. He showed that, depending on the reaction conditions (molar ratio of the starting materials and temperature of the reaction mixture), the type of interaction changes. A 1 : 3 mixture of triethylaminium and carbon tetrachloride is safe at 0°C, but explodes at 20°C. The mixture in molar proportions of 1 : 10 can be controlled not only at room temperature but also at 75–80°C. The main reaction products are chloroform, methylene chloride, and monochloro-substituted methane, ethane, and propane. These compounds are also formed in the reaction of ethylaluminium dichloride[139] with carbon tetrachloride. Diethylaluminium and carbon tetrachloride in

proportions of 1 : 5 react slowly with formation of chloroform and ethyl chloride. A mixture of diethylaluminium hydride and carbon tetrachloride in molar proportions of 1 : 3 explodes at 80°C, but when the reaction ratio is changed to 1 : 5 the reaction takes place smoothly. The sesquichloride reacts with carbon tetrachloride at a moderate rate in proportions of 1 : 10 but an equimolar mixture explodes at room temperature[127]. Reinheckel believes that these reactions have a free-radical mechanism. At the same time it has been shown[140] that tri-isobutylaluminium reacts with carbon tetrachloride, forming a trichloromethyl derivative:

$$R_3Al + CCl_4 \rightarrow RCl + R_2AlCCl_3 \rightarrow R_2AlCl + \ddot{C}Cl_2 .$$

The yield of di-isobutylaluminium chloride is 92% and that of isobutyl chloride 25%. The dichlorocarbene formed reacts with the initial organometallic compound or cyclohexene and gives rise to 7,7-dichlorononcarane in reactions where the olefin has been added.

The literature data discussed above lead to the conclusion that the initial stage in the reaction of organoaluminium compounds with polyhalogenomethanes, as for the lithium and magnesium compounds, is the formation of the corresponding intermediate halogenomethyl derivatives, which decompose with generation of carbenes. By virtue of their exothermic nature, these reactions are probably accompanied by the thermal decomposition of the organoaluminium compounds.

It has been suggested[141] that unstable halogenomethyl derivatives are formed in the reaction of trimethylthallium with polyhalogenomethanes: CHX_3 (X = Cl, Br, or I) and methylene dichloride and dibromide. The reaction products are methane and $(CH_3)_2TlX$. However, trimethylthallium does not react with carbon tetrachloride and methylene dichloride at room temperature. The reaction of dimethylthallium ethoxide with chloroform results in a quantitative yield of dimethylthallium chloride[141].

V. REACTIONS OF ORGANIC COMPOUNDS OF GROUP IV ELEMENTS

The majority of organic derivatives of non-transition elements (silicon, germanium, tin, and lead) react with polyhalogenomethanes in the same way as organomercury compounds, in the presence of initiators or catalysts. The reactivity increases from silicon to lead compounds. Organotitanium compounds, which have covalent Ti–C σ bonds, react with halogenomethanes much more readily.

1. Reactions of Organosilicon and Organogermanium Compounds

Organosilicon and organogermanium derivatives are fairly inert in relation to polyhalogenomethanes. Tetraphenylsilicon[142] does not react with carbon tetrachloride at the boiling point of the reaction mixture. Tributylgermanium hydride[143–145] reacts with carbon tetrachloride only at 200–220°C with formation of tributylgermanium chloride and chloroform.

The unusual behaviour of tetraethylsilicon in carbon tetrachloride solution on irradiation with ultraviolet light is of interest. Under these conditions, tetraethylsilicon is chlorinated without the abstraction of a radical with formation of chloroethyltriethylsilicon[146] (tetraphenylsilicon and methyltriphenylsilicon did not undergo any changes). The reactions of organosilicon compounds of the type R_4Si, R_3SiH, and R_6Si_2 with polyhalogenomethanes under the influence of organic peroxides have been described.

The main products of the reaction of tetraethylsilicon[146] with carbon tetrachloride in the presence of acyl peroxides are, as in the photochemical reaction, chloroethyltriethylsilicon (a mixture of α- and β-isomers) and chloroform. The free radicals formed in the decomposition of the initiator react with tetraethylsilicon:

$$R'^{\cdot} + (C_2H_5)_4Si \rightarrow R'H + (C_2H_5)_3Si\dot{C}_2H_4 , \quad (10)$$

$$(C_2H_5)_3Si\dot{C}_2H_4 + CCl_4 \rightarrow (C_2H_5)_3SiC_2H_4Cl + Cl_3C^{\cdot} , \quad (11)$$

$$Cl_3C^{\cdot} + (C_2H_5)_4Si \rightarrow CHCl_3 + (C_2H_5)_3Si\dot{C}_2H_4 .$$

In the presence of benzoyl peroxide organosilicon compounds containing double bonds[147] combine with $CXCl_3$ (X = H or Cl) via a free-radical mechanism:

$$R_3SiCH{=}CH_2 \xrightarrow{CXCl_3} R_3SiCHX - \dot{C}H_2CCl_3 . \quad (12)$$

A reaction analogous to reaction (12) has also been described for unsaturated organogermanium compounds[148]. Acetylene derivatives of silicon react with bromotrichloromethane and dibromodichloromethane on irradiation of the reaction mixture by ultraviolet light with formation of the corresponding bromochloropropenylsilanes[149,150].

The reaction of substituted silanes with $CXCl_3$ (X = H, Cl, or Br), carbon tetrabromide, and methylene dibromide has been investigated in the presence of benzoyl peroxide[151–157], t-butyl peroxide[154], and also catalysts—palladium[158], iron pentacarbonyl, or chloroplatinic acid[159]. In this process the polyhalogenomethane is reduced: CX_4 to CHX_3, CHX_3 to CH_2X_2, etc. In the presence of peroxycompounds the reactions proceed via a free-radical chain mechanism[151–157]:

$$(C_6H_5COO)_2 \rightarrow 2C_6H_5COO^{\cdot} ,$$

$$C_6H_5COO^{\cdot} + R_3SiH \rightarrow C_6H_5COOH + R_3Si^{\cdot} ,$$

$$R_3Si^{\cdot} + CH_nX_{4-n} \rightarrow R_3SiX + \dot{C}H_nX_{3-n} ,$$

$$(n=1, 2;\ X=Cl, Br)$$

$$\dot{C}H_nX_{3-n} + R_3SiH \rightarrow CH_{n+1}X_{3-n} + R_3Si^{\cdot} .$$

It has been shown by ESR[160] that the photochemical reaction of substituted silanes and also germanes and stamanes with carbon tetrachloride in the presence of t-butyl peroxide is accompanied by the formation of trichloromethyl radicals:

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO^{\cdot} ,$$

$$(CH_3)_3CO^{\cdot} + R_3EH \rightarrow (CH_3)_3COH + R_3E^{\cdot} ,$$

$$(E=Si, Ge, Sn)$$

$$R_3E^{\cdot} + CCl_4 \rightarrow R_3ECl + Cl_3C^{\cdot} .$$

Photolysis of triethylsilicon iodide in methylene dichloride, chloroform, or carbon tetrachloride solution leads to the formation of triethylsilicon chloride[161]. Polyhalogenomethanes can be arranged in the following sequence in terms of the ease of exchange of iodine for chlorine:

$$CCl_4 > CHCl_3 > CH_2Cl_2 .$$

It is suggested that this exchange takes place via a free-radical chain mechanism.

The reaction of diphenylsilane with methylene di-iodide in the presence of olefins[162] at 189°C is accompanied by the formation of cyclopropanes (17–38%).

The reaction of hexamethyldisilane[163] with carbon tetrachloride in the presence of benzoyl peroxide (at 80°C) or t-butyl peroxide (at 129°C) takes place without the dissociation of the Si–Si bond. It is suggested that (pentamethyldisilyl)methyl radicals participate in the reaction:

they recombine or abstract a chlorine atom from carbon tetrachloride. The primary process is the decomposition of the initiator into radicals, which then react with the initial silicon compound:

$$R^{\cdot} + (CH_3)_6Si_2 \rightarrow R'H + (CH_2)_5Si_2\dot{C}H_2,$$

$$2\,(CH_3)_5Si_2\dot{C}H_2 \rightarrow (CH_3)_5Si_2CH_2CH_2Si_2(CH_3)_5,$$

$$(CH_3)_5Si_2\dot{C}H_2 + CCl_4 \rightarrow (CH_3)_5Si_2CH_2Cl + Cl_3C^{\cdot},$$

$$Cl_3C^{\cdot} + (CH_3)_6Si_2 \rightarrow CHCl_3 + (CH_3)_5Si_2\dot{C}H_2.$$

2. Reactions of Organotin and Organolead Compounds

Organotin and organolead compounds have almost the same reactivity with respect to polyhalogenomethanes. The chemical reactivity of these compounds depends on their type. The hydrides R_3MH react most readily, compounds of the type R_6M_2 react with more difficulty, and the reaction involving R_4M (M = Sn or Pb) is more difficult still. The tetra-aryl organometallic compounds[142] do not react with carbon tetrachloride at the boiling point of the reaction mixture. Tetra-alkyl compounds of tin[164] also do not react with carbon tetrachloride at 100°C. In contrast to the alkoxy-compounds of mercury, monoalkoxy-derivatives of tin are inert with respect to chloroform. Trimethyltin t-butoxide did not react with chloroform on heating the reaction mixture at 140°C for 1 h.[81] However, amino-compounds of the type $R_3SnNR'_2$ undergo an exothermic reaction with CHX_3 (X = Cl or Br), forming trihalogenomethyl derivatives of the organometallic compounds[165-167]:

$$R_3SnNR'_2 + CHX_3 \rightarrow R_3SnCX_3 + R'_2NH.$$

When a mixture of tetra-alkyl compounds of tin with trifluoroiodomethane is heated, fluoroform is formed. In the reaction of tetramethyl-lead with the above halogeno-derivative, a methyl group of the organometallic compound is exchanged for a trifluoromethyl group[168,169], which results in the formation of trifluoromethyltrimethyl-lead $(CH_3)_3PbCF_3$. The reaction takes place similarly under the influence of ultraviolet light. It is suggested that the trifluoromethyl derivative of lead is formed by a free-radical mechanism.

The photochemical reactions of organotin compounds of the type R_4Sn (R = CH_3,[170,171] C_2H_5,[171] n-C_3H_7,[170,171] or C_6H_5[172]) with carbon tetrachloride[171,172] and chloroform[170-172] have been investigated in greater detail. The monochloride and dichloride of alkyl- or aryl-tin derivatives, hydrocarbons, and hexachloroethane were isolated as the main products. In the reaction of the alkylated organometallic compounds with carbon tetrachloride, chloroform and 1,1,1,3-tetrachloroalkanes [see reaction (7)] are also formed. The first step in the reaction is photolysis of the organometallic compound to R and R_3Sn radicals or of carbon tetrachloride to Cl and Cl_3C radicals. Trialkyl(aryl)stannyl radicals react with chloroform or carbon tetrachloride. The resulting $CXCl_2$ radicals (X = H or Cl) react with the alkylated organometallic compounds:

$$\dot{C}XCl_2 + R_4Sn \rightarrow CHXCl_2 + R_3Sn\dot{R}_{-H} \rightarrow R_3Sn^{\cdot} + \underset{\text{(olefin)}}{R_{-H}}.$$

In contrast to the corresponding silicon derivatives [reactions (10) and (11)], the organotin radicals with an unpaired electron at the carbon atom decompose and split off an olefin. Under the reaction conditions, the monochloride of trialkyl(aryl)tin also interacts with polyhalogenomethanes forming R_2SnCl_2.

It is interesting to note that the photolysis of asymmetric tin compounds containing alkyl and aryl groups is accompanied by the abstraction of aryl radicals. Following the reaction of diethyldiphenyltin and dibenzyldiphenyltin[173] with carbon tetrachloride and chloroform, the dichloride of the corresponding dialkyltin was isolated from the reaction mixture.

The photochemical reactions of organolead compounds with polyhalogenomethanes have been hardly investigated. It has been noted[172] that tetraphenyl-lead reacts with chloroform and carbon tetrachloride similarly to diphenylmercury. Diphenyl-lead dichloride, lead chloride, benzene or chlorobenzene, hexachloroethane, and, in the case of chloroform, also metallic lead were isolated from the reaction mixture.

The photolysis of triphenyltin and triphenyl-lead azides in methylene dichloride solution[174] is accompanied by the generation of $(C_6H_5)_3M$ radicals, which react with the halogenomethane, forming triphenyltin or triphenyl-lead chlorides (51–75%).

Oxygen and organic peroxides initiate the reactions of organotin and organolead compounds. The alkyl derivatives of tin[164] R_4Sn (R = C_2H_5, n-C_3H_7, or iso-C_3H_7) react in an atmosphere of oxygen with carbon tetrachloride at 100°C, forming trialkyltin, chloroform, and 1,1,1,3-tetrachloroalkanes as the main products. The organotin compound with a secondary alkyl group (tetraisopropyltin) reacts with carbon tetrachloride at a lower temperature (60°C). It has been noted[175] that oxygen greatly accelerates the reaction of tetramethyl-lead with carbon tetrachloride, which is accompanied by the formation of a white precipitate. The initiating effect of oxygen is associated with the formation of free radicals in the oxidation of the initial tin and lead compounds[176].

The reactions of many organotin compounds (tetraethyltin[177], diethyldimethyltin[177], tetraphenyltin[178], and triethyltin chloride[177]) with carbon tetrachloride in the presence of benzoyl peroxide have been investigated. The reaction of tetraethyltin with carbon tetrachloride at 75–90°C yields triethyltin chloride, diethyltin dichloride, chloroform, ethylene, ethane, benzoic acid, carbon dioxide, and many other compounds[177]. Under these conditions, triethyltin chloride reacts with carbon tetrachloride similarly to tetraethyltin, forming the same products. Tetraphenyltin undergoes complete dearylation. Tin(IV) chloride, chlorobenzene, hexachloroethane and benzoic and phthalic acids were isolated from the reaction mixture[178]. Tetraphenyl-lead reacts with carbon tetrachloride in the presence of benzoyl peroxide, forming diphenyl-lead dichloride and dibenzoate[178]. These reactions are initiated by the free radicals formed as a result of the decomposition of benzoyl peroxide. The above processes have free-radical chain mechanisms.

Organotin compounds with an unsaturated alkyl group (triethylvinyltin[179] and triphenylvinyltin[180]) combine with polyhalogenomethanes $CXCl_3$ [X = H, Cl, or Br; see the analogous reaction (12)] in the presence of benzoyl peroxide.

The reactions of tin and lead compounds with carbon tetrachloride in the presence of catalysts have been described. In the presence of bismuth trichloride (0.5–1.0 mole per mole of the organometallic compound) the tetraphenyl compounds react with carbon tetrachloride at the boiling point of the reaction mixture, forming chlorobenzene, triphenyltin chloride or triphenyl-lead chloride, and diphenyl-lead dichloride. Bismuth trichloride was recovered quantitatively from the reaction mixture[142]. Alkyl[181,182] and aryl[183,184] compounds of tin also undergo

dealkylation (dearylation) at a comparatively low temperature in the presence of bismuth and aluminium chlorides in chloroform solution.

In the presence of aluminium chloride or boron trifluoride tetramethyl- and tetraethyl-lead[185] react with methylene dibromide, forming compounds having the composition $R_3PbCH_2PbR_3$.

As the number of alkyl (aryl) groups linked to the metal atom decreases, the reactivity of the organotin and organolead compounds in relation to polyhalogenomethanes rises. In contrast to the tetra-alkyl derivatives, hexacyclohexyldilead reacts with carbon tetrachloride even at room temperature, forming tricyclohexyl-lead chloride and dicyclohexyl-lead dichloride[175]. Possibly a trichloromethyl derivative of lead is formed as an intermediate in this process:

$$(C_6H_{11})_3PbPb(C_6H_{11})_3 + CCl_4 \rightarrow (C_6H_{11})_3PbCl + (C_6H_{11})_3PbCCl_3 .$$

In the presence of oxygen the reaction terminates much faster. Then the main products are the chlorides of tricyclohexyl-lead and dicyclohexyl-lead (in nearly equimolar proportions), cyclohexyl chloride, hexachloroethane, and carbon dioxide. In an atmosphere of oxygen this organometallic compound reacts vigorously with carbon tetrabromide and is quantitatively converted into dicyclohexyllead dibromide. The problem of the involvement of trihalogenomethyl compounds in these reactions remains unresolved. However, the analogous trihalogenomethyl derivative of tin has been isolated from the reaction mixture in the reaction between hexamethylditin and trifluoroiodomethane. The reaction takes place on heating[186] to 80°C or on irradiation with ultraviolet light[187,188]:

$$(CH_3)_3SnSn(CH_3)_3 + CF_3I \rightarrow (CH_3)_3SnI + (CH_3)_3SnCF_3 .$$

It is suggested that trifluoromethyltrimethyltin is formed in these processes by a free-radical mechanism:

$$R_3SnSnR_3 \rightarrow 2R_3Sn^{\cdot},$$
$$R_3Sn^{\cdot} + CF_3I \rightarrow R_3SnCF_3 + I^{\cdot},$$
$$I^{\cdot} + R_3SnSnR_3 \rightarrow R_3SnI + R_3Sn^{\cdot} .$$

One cannot exclude the possibility of the formation of an intermediate complex of the organometallic compound with trifluoroiodomethane.

The reactions of hexa-alkylditin compounds with carbon tetrachloride are initiated by oxygen and acyl peroxides[177,189]. In an atmosphere of oxygen, hexaethylditin reacts with carbon tetrachloride forming a mixture of triethyltin and diethyltin chloride[177]. The products of the reaction carried out in the presence of benzoyl peroxide are ethane, ethylene, butane, carbon dioxide, chloroform, triethyltin chloride and benzoate, and diethyltin dichloride[177,189]. These processes have a free-radical mechanism. The high yields of chloroform and ethylene indicate the abstraction of hydrogen atoms from the ethyl group of the organometallic compound by trichloromethyl radicals:

$$Cl_3C^{\cdot} + (C_2H_5)_6Sn_2 \rightarrow CHCl_3 + (C_2H_5)_5Sn_2\dot{C}_2H_4$$
$$\downarrow$$
$$(C_2H_5)_3Sn^{\cdot} + C_2H_4 + (C_2H_5)_3Sn ,$$
$$(C_2H_5)_3Sn^{\cdot} + CCl_4 \rightarrow (C_2H_5)_3SnCl + Cl_3C^{\cdot},$$
$$(C_2H_5)_2Sn \xrightarrow{CCl_4} (C_2H_5)_2SnCl_2 .$$

In the presence of freshly precipitated copper, hexaalkylditin compounds react with carbon tetrachloride under milder conditions[190]. Hexaethylditin and hexabutylditin react with carbon tetrachloride at room temperature, forming trialkyltin chloride, chloroform, hexachloroethane, copper chlorides, and coloured organotin compounds.

The reactions of organotin hydrides R_3SnH with polyhalogenomethanes proceed in the absence of initiators or catalysts. The reaction of triphenyltin hydride[145,191] with carbon tetrachloride is exothermic. This results in quantitative yields of chloroform and triphenyltin chloride. Triphenyltin hydride reacts less vigorously with chloroform and methylene dichloride[176]. The reaction leads to the reduction of chloroform to methylene dichloride and of the latter to methyl chloride. Polyhalogenomethanes can be arranged in the following sequence in terms of the rates of the above reactions:

$$CCl_4 > CHCl_3 > CH_2Cl_2 .$$

Alkyltin hydrides also reduce polyhalogenomethanes[192-194]. Tributyltin hydride reduces carbon tetrachloride to chloroform (about 85%) and the latter to methylene dichloride[192]. The above organometallic compound reacts with bromoform and tribromofluoromethane[192], forming tributyltin bromide (up to 95%) and methylene dibromide (62%) and dibromofluoromethane (69%) respectively.

The chemical reactivity of the hydrides depends on the nature of the alkyl group. The rate of reaction of tributyltin hydride with carbon tetrachloride and chloroform is appreciably lower than that of trimethyltin hydride[193].

Owing to their low thermal stability, organolead hydrides have been little investigated. They are much more reactive than the corresponding tin hydrides. The reaction of trialkyltin hydrides with carbon tetrachloride involves the reduction of the latter to chloroform[195].

The mechanism of the reaction of organolead and organotin hydrides with polyhalogenomethanes is insufficiently clear. It is believed that these reactions have a free-radical mechanism.

3. Reactions of Organotitanium Compounds

Among the organometallic compounds of Group IV elements, titanium derivatives have been most thoroughly investigated. In the present review we shall discuss the reactions with polyhalogenomethanes of compounds where an organic group is bound covalently to the titanium atom, i.e. compounds with metal–carbon σ bonds.

The reactions of di- and tetra-valent titanium derivatives with chloroform and carbon tetrachloride were investigated in greatest detail by Razuvaev and coworkers. Titanium(II) derivatives (diphenyltitanium and cyclopentadienylphenyltitanium) are thermally stable. Their reactions with chloroform and carbon tetrachloride involve the splitting off of phenyl groups and the oxidation of titanium to the tetravalent state[196,197]. The products of the reaction of diphenyltitanium[196] with chloroform at room temperature are titanium tetrachloride, benzene, and biphenyl. Cyclopentadienyltitanium trichloride ($C_5H_5TiCl_3$) is formed in the reactions of cyclopentadienylphenyltitanium[197]. Probably the primary step in the reaction is the formation of a complex of the organometallic compound and the polyhalogenomethane, the subsequent reaction of which involves the generation of phenyl radicals.

Compounds of tetravalent titanium of the type R_nTiX_{4-n} ($n = 1, 2, 3$, or 4) have been investigated in greatest detail. They are less stable than the organic derivatives of divalent titanium.

The reaction of tetramethyl titanium[198] with gaseous trifluoroiodomethane in 2 : 1 ethyl ether–hexane solution at −78°C results in the formation of trimethyltitanium iodide and methyl iodide. Tetramethyltitanium-ether

reacts with carbon tetrachloride, forming methyl chloride, methane, and titanium tetrachloride[199]. The products of the reaction of tetramethyl titanium with carbon tetrachloride in ethereal solution in the presence of mercury indicate a homolytic mechanism of this reaction[200]:

$$(CH_3)_4Ti + 2CCl_4 + Hg \rightarrow 3CH_4 + CH_3HgCl + TiCl_4 + Cl_3C^{\cdot}.$$

This is confirmed also by the fact that the analogous system tetraphenyl-lithium–carbon tetrachloride initiates the low-temperature free-radical polymerisation of vinyl chloride[201].

Cyclopentadienyltriphenyltitanium reacts with chloroform between −70° and −50°C. This results in an almost quantitative yield of benzene and cyclopentadienyltitanium trichloride[202].

The reactions of dicyclopentadienyldimethyltitanium[203] and dicyclopentadienyldiphenyltitanium[204,205] with carbon tetrachloride at 60–80°C are accompanied by the dissociation of σ bonds and the retention of the sandwich group. The products are dicyclopentadienyltitanium dichloride (about 75%), hexachloroethane, and respectively methyl chloride (95%) and chlorobenzene. In the thermal reaction of chloroform with $(C_5H_5)_2Ti(CH_3)_2$, dicyclopentadienyltitanium dichloride (75%) and methane (80%) are also formed. Dibenzyldicyclopentadienyltitanium reacts with chloroform similarly[203]. The thermal and photochemical reactions of $(C_5H_5)_2Ti(C_6H_5)_2$ with chloroform are accompanied by the formation of $(C_5H_5)_2TiCl_2$ and benzene[204–206]. It is suggested that dicyclopentadienyltitanium is an intermediate in these reactions:

$$(C_5H_5)_2TiR_2 \rightarrow (C_5H_5)_2Ti + 2R^{\cdot},$$
$$R^{\cdot} + CXCl_3 \rightarrow RX + Cl_3C^{\cdot},$$
$$(X = H, Cl)$$
$$(C_5H_5)_2Ti \xrightarrow{CXCl_3} (C_5H_5)_2TiCl_2.$$

The reactions of organotitanium compounds of this type with polyhalogenomethanes are initiated by oxygen[204,205]. The reaction of dicyclopentadienyldiphenyltitanium with carbon tetrachloride takes place in the presence of oxygen at a lower temperature (45–55°C). Then phosgene, biphenyl, and small amounts of phenol are formed together with dicyclopentadienyltitanium dichloride and chlorobenzene.

Reactions of titanium compounds of the type $RTiCl_3$ (R = CH_3 or C_6H_5) with carbon tetrachloride and chloroform have been described. Phenyltitanium trichloride reacts with chloroform, forming benzene and biphenyl. Chlorobenzene was not detected in the reaction with carbon tetrachloride[207]. The reaction of methyltitanium trichloride[208–210] with carbon tetrachloride leads to the formation of methyl chloride. Data indicating a free-radical mechanism of these reactions have been adduced[209].

VI. REACTIONS OF TWO-ELEMENT ORGANIC COMPOUNDS

The chemistry of organic compounds with two and more non-organic elements, i.e. the chemistry of compounds with carbon–element–element bonds, is developing vigorously at the present time. The previous section dealt with reactions of two-element organic compounds of the type $R_3E–ER_3$ (E = Si, Sn, or Pb) with polyhalogenomethanes. It is useful to discuss also reactions of organic derivatives having bonds between two different elements. It should only be noted that, despite the large variety of compounds of this type which have been obtained, their reactivity in relation to polyhalogenomethanes has been scarcely investigated. There are only a few data on the reactions of the compounds R_3EM (E = Si, Ge, Sn, or Pb and M = Li or Na) with alkyl halides.

The reactions of triphenylsilyl-lithium with polyhalogenomethanes have been investigated in greater detail. The reaction of this compound with methylene dichloride[211–213] results in the formation of hexaphenyldisilane, methyltriphenylsilane, chloromethyltriphenylsilane, and bis(triphenylsilyl)methane in proportions which depend on the reaction conditions. It is suggested[213] that chloromethyl derivatives of lithium, which serve as a source of carbenes, are formed in these reactions. Their mechanism may be represented as follows:

$$R_3SiLi + CH_2Cl_2 \rightarrow R_3SiCl + CH_2ClLi \rightarrow \ddot{C}H_2 + LiCl,$$
$$R_3SiCl + R_3SiLi \rightarrow R_3SiSiR_3 + LiCl,$$
$$R_3SiLi + \ddot{C}H_2 \rightarrow R_3SiCH_2Li,$$
$$R_3SiCH_2Li \begin{cases} \xrightarrow{CH_2Cl_2} R_3SiCH_2Cl + CH_2ClLi, \\ \xrightarrow{R_3SiCl} R_3SiCH_2SiR_3 + LiCl, \end{cases}$$
$$R_3SiCH_2Li \xrightarrow{H_2O} R_3SiCH_3.$$

Methylene di-iodide reacts similarly. The reaction of triphenylsilyl-lithium with methylene dibromide leads to the formation of hexaphenyldisilane (42–60% with respect to Ph_3SiLi), methyltriphenylsilane (up to 40%), and bromomethyltriphenylsilane (about 10%) with respect to methylene dibromide).

The products of the reaction of triphenylsilyl-lithium[212,213] with CHX_3 (X = Cl, Br, and I) are methyltriphenylsilane, hexaphenyldisilane, mono- and di-halogenomethyltriphenylsilanes, bis(triphenylsilyl)methane, and triphenylsilane. Probably the initial stage is the following process:

$$R_3SiLi + CHX_3 \begin{cases} \rightarrow R_3SiH + CX_3Li \rightarrow \ddot{C}X_2 + LiX, \\ \rightarrow R_3SiX + CHX_2Li \rightarrow \ddot{C}HX + LiX. \end{cases}$$

It has been shown that the yield of reaction products depends on the reactant ratio. In the reaction between the organometallic compound and methyl iodide in molar proportions of 3 : 1, hexaphenyldisilane (60.5% with respect to Ph_3SiLi), bis(triphenylsilyl)methane (19.5%), and methyltriphenylsilane (24% with respect to iodoform) are formed. A change in reactant ratio to 2 : 1 leads to the formation of hexaphenyldisilane and almost equimolar amounts of monoiodomethyl- and di-iodomethyl-triphenylsilanes.

Hexaphenyldisilane (56–73%) and dichloromethyltriphenylsilane (11–42%) are formed at −60°C in the reaction of triphenylsilyl-lithium[213] with carbon tetrachloride. The reaction with carbon tetrabromide is much more complex.

The reactions of triphenylgermylsodium[214–216] with methylene dichloride, chloroform, and carbon tetrachloride have been carried out in liquid ammonia and in ether. The main product of the reaction with methylene dichloride is bis(triphenylgermyl)methane. The above organometallic compound reacts with chloroform and carbon tetrachloride in ethereal solution in a more complex manner, forming mainly hexaphenyldigermane[215,216].

It is interesting to note that bis(triethylgermyl)cadmium[217], like the organometallic alkyl derivatives R_2Cd, reacts vigorously with carbon tetrachloride. The reaction mixture explodes at room temperature. Triethylgermanium chloride (41%), dichlorobis(triethylgermyl)methane (55%), and cadmium chloride (91.5%) are formed in the reaction carried out at −75°C. The mechanism of the reaction has not been elucidated. It is suggested that

dichlorocarbene is involved in the reaction. Probably derivatives of the type $R_3GeCdCCl_3$ or R_3GeCCl_3 are produced as intermediates.

The corresponding mercury compound (like R_2Hg) proved to be less reactive with respect to carbon tetrachloride. The photochemical reaction[218] of bis(triethylgermyl)mercury with carbon tetrachloride involves the formation of mercury (60%), triethylgermanium chloride (36%), and hexachloroethane.

Tris(trimethylsilyl)thallium reacts with chloroform, forming bis(trimethylsilyl)thallium chloride, but does not react with methylene dichloride[219].

The reaction of tris(trimethylsilyl)silane with carbon tetrachloride leads to the formation of tris(trimethylsilyl)silicon chloride and chloroform[220]:

$$[(CH_3)_3Si]_3SiH + CCl_4 \xrightarrow{\text{reflux.}} [(CH_3)_3Si]_3SiCl + CHCl_3 .$$

The reactions of trialkyl(aryl)stannylsodium with methylene dichloride[221,222], chloroform[223-225], and carbon tetrachloride[222,223] have been investigated. The reaction with methylene dichloride results in the formation of the corresponding bis[trialkyl(aryl)stannyl]methanes. The reaction with chloroform is more complex. Trimethylstannylsodium and triphenylstannylsodium react with carbon tetrachloride, forming hexamethyl- and hexaphenylditin.

The reaction of triphenylplumbyl-lithium with methylene dichloride, chloroform, and carbon tetrachloride in tetrahydrofuran solution at −60°C leads to the formation of a high yield of the corresponding bis-, tris-, and tetrakis-(triphenylplumbyl)methanes[226]. The reactions with bromochloromethane yield[227,228] a mixture of compounds, the main component of which is a derivative of the type $R_3Pb(CH_2)_nPbR_3$.

Prolonged photolysis (100 h) of the complex compounds lithium or potassium tetraphenylborates in chloroform solution is accompanied by the formation of benzene, biphenyl, triphenylboron and respectively lithium or potassium chlorides[229]. It is suggested[230] that these reactions take place with participation of phenyl radicals.

The above review shows that organic derivatives with two "non-organic" elements react with polyhalogenomethanes in a fairly complex manner. The mechanism of these processes is still not entirely clear.

VII. REACTIONS OF ORGANIC COMPOUNDS OF GROUP V ELEMENTS

The reactions of organic compounds of phosphorus, arsenic, antimony, and bismuth with polyhalogenomethanes have been described for derivatives of the type R_3E and R_5E. The first data on the reactivity of organophosphorus compounds with respect to polychloromethanes[231-233] were obtained in studies on the chemical properties of triethylphosphine. In particular it was stated that this compound forms an adduct with carbon tetrachloride having the composition $3(C_2H_5)_3P.CCl_4$.

Organic derivatives of tervalent elements combine with trichloroiodomethane[234], forming an adduct with the composition $R_3E.CCl_3I$. The reactions were carried out in ether with the reaction mixture cooled to −46°C. The following compounds were obtained in this way (the melting points and decomposition temperatures are indicated in brackets): $(CH_3)_3P.CCl_3I$ (10°C, decomposes), $(C_6H_5)_3P.CCl_3I$ (72°C, 110°C), $(CH_3)_3As.CCl_3I$ (39°C, 95°C), $(C_6H_5)_3As.CCl_3I$ (−30°C, 100°C), and $(CH_3)_3Sb.CCl_3I$ (5°C, 82°C).

Triphenylantimony in ether does not react with trichloroiodomethane at temperatures ranging from −78° to 20°C. Nor does it react with chloroform when the reaction mixture is illuminated. However, photolysis of triphenylbismuth in chloroform solutions is accompanied by the formation of bismuth trichloride, bismuth, and benzene. Bismuth trichloride and biphenyl are formed in the photochemical reaction with carbon tetrachloride[172].

It has been noted[234] that trimethylphosphine does not react with carbon tetrachloride. However, later it was shown[235] that trialkylphosphines react with carbon tetrachloride in ether when the temperature of the reaction mixture is −10°C. The formation of phosphonium compounds is suggested:

$$R_3P + CCl_4 \rightarrow R_3P\langle^{CCl_3}_{Cl} \qquad (R = n\text{-}C_4H_9,\ n\text{-}C_5H_{11} \text{ etc.}) .$$

In the presence of methanol the latter form trialkylphosphine oxides, methyl chloride, and chloroform:

$$R_3P\langle^{CCl_3}_{Cl} + CH_3OH \rightarrow R_3PO + CH_3Cl + CHCl_3 .$$

Similar results were obtained somewhat earlier[236] in the reaction of triphenylphosphine with carbon tetrachloride or bromotrichloromethane in the presence of ethanol. The mechanism of the reactions of triphenylphosphine with carbon tetrachloride and carbon tetrabromide has been discussed[237-239]. It is believed that a phosphonium compound, formed as a result of the nucleophilic attack by phosphorus on the halogen, is an intermediate in the reaction:

$$R_3\ddot{P}\text{—}\overset{X}{\underset{CX_3}{|}} \rightarrow R_3P^{+}\cdots X^{-}\cdots CX_3 \rightarrow R_3P\langle^{X}_{CX_3} , \quad (X = Cl^{237,238}, Br^{239}) \qquad (13)$$

$$R_3P\langle^{X}_{CX_3} + R_3P \rightarrow R_3P{=}CX_2 + R_3PX_2 .$$

The presence of dihalogenomethylenetriphenylphosphorane was established on the basis of the products of the reaction with carbonyl compounds, in particular with benzaldehyde[237,239]:

$$R_3P{=}CX_2 + C_6H_5CHO \rightarrow R_3PO + C_6H_5CH{=}CX_2 .$$

Triphenylphosphine[236] does not react with chloroform and bromoform on heating the reaction mixture to 80°C, but does react with bromoform in the presence of benzoyl peroxide[240]. The initiating effect of the latter was not confirmed in a subsequent investigation[236]. Triphenylphosphine reacts with bromoform at 150°C, forming dibromomethyltriphenylphosphonium bromide[236]:

$$R_3P + CHBr_3 \rightarrow [R_3PCHBr_2]^+Br^- .$$

The reactions of alkyl esters of alkyl- or aryl-phosphinous acids with carbon tetrachloride have been investigated[235,241]. The aryl derivatives[241] react according to the mechanism

$$Ar_2POR + CCl_4 \rightarrow Ar_2P(O)CCl_3 + RCl ,$$
$$(R = C_2H_5,\ n\text{-}C_3H_7) .$$

Reactions of compounds of the type $(RO)_3P$ with polyhalogenomethanes are not considered in this review.

The reaction of amino-substituted alkylphosphines with carbon tetrachloride results in the formation of 1,1,1-trichloroalkanes[242]. Trichlorobutane was isolated in 50% yield from the reaction mixture of bis(diethylamino)propylphosphine with carbon tetrachloride.

The reactions of organic derivatives of the elements of the type R_5E with polyhalogenomethanes have been investigated for pentaphenylphosphorane and pentaphenylantimony. Pentaphenylphosphorane reacts with chloroform and carbon tetrachloride at room temperature. Wittig and Geissler[243] reported that the reaction of this compound with chloroform has an ionic mechanism and involves the formation of tetraphenylphosphonium chloride and benzylidene chloride. In a more detailed study of the reaction of pentaphenylphosphorane with chloroform and carbon tetrachloride by Razuvaev and coworkers[244-248], it was established that these processes take place with participation of free radicals. This results in the formation of a quantitative yield of tetraphenylphosphonium chloride and of chlorobenzene (64%) in the reaction with carbon tetrachloride and of benzene (60–65%) in the reaction with chloroform. Benzylidene dichloride was not detected.

Pentaphenylantimony reacts similarly with chloroform and carbon tetrachloride[249]. Tetraphenylantimony chloride, biphenyl, and respectively benzene or chlorobenzene are formed in thermal reactions (100°C, 20–25 h) and in photolysis. The mechanism of these processes may be represented as follows:

$$R_5E \rightarrow R_4E^{\cdot} + R^{\cdot},$$
$$(E=P, Sb)$$
$$R_4E^{\cdot} + CXCl_3 \rightarrow R_4ECl + \dot{C}XCl_2,$$
$$(X=H, Cl)$$
$$R^{\cdot} + CXCl_3 \rightarrow RX + Cl_3C^{\cdot},$$
$$2R'' \rightarrow R'-R'.$$
$$(R'=Cl_3C, CXCl_2, R)$$

The photolysis of t-butylperoxytetraphenylantimony in carbon tetrachloride and chloroform solutions was investigated recently[250]. The reaction with carbon tetrachloride involves predominantly the dissociation of the Sb–O bond and the formation of tetraphenylantimony chloride (up to 83%). In the reaction with chloroform tetraphenylantimony chloride (41%), tetraphenylantimony oxide (40%), t-butyl alcohol (44%), and benzene (17%) were obtained, together with phenol (6%) and acetone (10%) as side products. These compounds are formed owing to the dissociation of the Sb–O and O–O bonds in the initial compound.

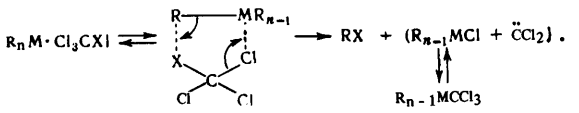
Thus the mechanism of the reaction of organic derivatives of the elements of the type R_3E with polyhalogenomethanes differs radically from the mechanism of the corresponding reactions with compounds of the pentavalent elements R_5E.

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Organic derivatives of the elements can be divided into two groups in terms of their reactivity with respect to polyhalogenomethanes. The first includes organic compounds of alkali and evidently alkaline earth metals and Group III metals and also the alkyl compounds of zinc and cadmium, derivatives of divalent tin, and true organometallic derivatives of transition metals (in particular divalent titanium compounds). Their reactions with alkyl halides do not require initiation. Probably the primary step in the reaction of these organometallic compounds with polyhalogenomethanes is nucleophilic attack by the halogen on the metal accompanied by the formation of a complex and then of the corresponding halogenomethyl organometallic derivatives:

$$R_nM + CXCl_3 \rightleftarrows [R_nM \cdot Cl_3CX] \rightarrow R_{n-1}MCCl_3 + RX.$$
$$(X=H, Cl, Br, I)$$

One cannot exclude the possibility that the compound reacts via a five-membered cyclic transition state with formation of the corresponding carbene and its subsequent insertion into the metal–halogen bond formed:



The insertion of carbenes into the metal–halogen bond is used as one of the methods for synthesising halogenomethyl organometallic compounds. Possibly the reaction of the halogenomethyl complex formed with certain organometallic compounds (in all probability with divalent titanium compounds) is associated with the generation of free radicals.

It is striking that the reactions of the majority of organometallic compounds of this group with polyhalogenomethanes are exothermic. Owing to the lack of kinetic data, the mechanism of these reactions still remains insufficiently elucidated.

The addition of polyhalogenomethanes of the type CYX_3 (Y = H, Cl, Br, or I; X = Cl or Br) to compounds of tervalent Group V elements R_3E (E = P, As, or Sb) evidently takes place as a result of nucleophilic attack by the element on the halogen [reaction (13)], which leads to the formation of the corresponding halogenomethyl derivatives.

The second group includes the aryl derivatives of zinc and cadmium, organic compounds of mercury (R_2Hg), titanium, tin, and lead of the type R_4M, compounds of silicon and germanium, and compounds of pentavalent phosphorus, arsenic, antimony, and bismuth. These compounds are less reactive. Their reactions with polyhalogenomethanes takes place on heating, irradiation with light, or in the presence of initiators, and clearly have a distinct free-radical mechanism.

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Institute of Chemistry at Gorky University