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Review

REACTIONS OF GROUP IVB ORGANOBIMETALLIC COMPOUNDS WITH ELECTROPHILIC REAGENTS

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INTRODUCTION

The chemistry of organobimetallic compounds of the IVB group (OBMC, general formula $R^1R^2R^3MM'R^4R^5R^6$, with M,M' = Si, Ge, Sn, Pb) is an active field of study. Nucleophiles, free radicals, alkali and alkaline-earth metals have been shown to react with OBMC, generally with M-M bond breaking. On the other hand, electrophiles are capable of splitting both M-M and M-C bonds, depending on the nature of the OBMC and the reagent involved. Until now there has been no analytical review of the reactions of OBMC with electrophiles, although this field is, beyond doubt, of theoretical and practical interest.

There are several reviews and monographs dealing with the chemistry of M-M bond compounds. For example, disilanes were discussed in the reviews [1-4] and books [5]; reactions of digermanes were mentioned in reviews [6,7]; the tin-containing OBMC - in the review [8] and monographs [9]; diplumbanes - in monograph [10]. A number of more specific review papers concerning OBMC chemistry was published [11]; see also [12]. Unfortunately most of these reviews are out of date now; some are not comprehensive. The reaction mechanisms and reactivity aspects are rather poorly discussed in the majority of reviews.

The present review deals with the reactions of OBMC with electrophilic reagents, the data being subdivided according to the types of electrophiles. Within each Section the data are presented (as far as it is possible) in the following sequence: Si - Ge - Sn - Pb. In Section III considerable attention is paid to the disproportionation reactions of the R_5M_2X and $R_4M_2X_2$ derivatives (involving α-elimination of the bivalent intermediates R_2M), which is essential for understanding the detailed reaction mechanisms of tin and lead OBMC with Lewis acids, including Lewis-acid-induced disproportionation of Sn_2R_6 and Pb_2R_6. The reactions of OBMC with (and catalyzed by) transition metal complexes, as well as the processes of carbene (and their analogues - $GeCl_2$, SO_2, etc.) inclusion, fall beyond the scope of the present review. Generally, principal emphasis will be placed on the mechanisms of the reactions studied.

I. HALOGENS

Halogenation of many OBMC was carried out. In all cases M-M bond breaking was observed, while the M-C bonds are usually not affected:

$$R^1R^2R^3M\text{-}M^1R^4R^5R^6 + Hal\text{-}Hal^1 \longrightarrow R^1R^2R^3MHal + R^4R^5R^6M^1Hal$$

Below are listed the OBMC and Hal_2 which react according to the preceding Equation: Si_2Me_6-Cl_2, Br_2, I_2 [31,32]; $Me_2EtSiSiMeEt_2$ - Br_2 [32]; Si_2Et_6 - Br_2, I_2 [35]; $ClCH_2(SiMe_2)_2Cl$-Br_2 [86]; Ph,Me, Cl-containing disilanes - Cl_2 [36]; $Et_3SiGePh_3$ and $Ph_3GeSnMe_3$ - Br_2 [34]; $Ph_3SiSnMe_3$ - Br_2 [37]; Ge_2Et_6 - Br_2 [38]; Ge_2Vy_6 - Br_2 and I_2 [95]; $(Me_2GeVy)_2$ - I_2 [96]; mixed alkylmethyldigermanes - Br_2 [39]; $(R_2GeCl)_2$ - Hal_2 [79]; $Et_3GeGeEtBuCl$ and $ClEt_2GeGeEt_2Bu$ - Cl_2 [80]; $Ph_3GeSn(OAc)_3$ - Br_2 [40]; $GeSn(OAc)_6$ - I_2 [40]; Sn_2Me_6 - Br_2 and I_2 [24,42]; Sn_2Et_6 - I_2 [225]; Sn_2Bu_6 - Cl_2 [44]; $Sn_2(i\text{-}Bu)_6$ - I_2 [54]; $Sn_2(c\text{-}C_6H_{11})_6$ - Br_2 and I_2 [45,49]; $(c\text{-}C_6H_{11})_3SnSn(i\text{-}Pr)_3$ - Br_2 [136]; $Sn_2(CH_2Ph)_6$ - I_2 [46]; Sn_2Ph_6 - Br_2 and I_2 [47,48,139]; $Sn_2(4\text{-}ClC_6H_4)_6$ - Br_2 and I_2 [50]; Et_5Sn_2Cl - Br_2 [55]; $(PhCO_2SnPh_2)_2$, $(PhCO_2SnBu_2)_2$ and $(Bu_2SnOAc)_2$ - Br_2 [55-57]; $(Cl_2SnOAc)_2$ - Cl_2 [58]; $Sn_2(OAc)_6$ - Br_2 [58]. The thermochemistry of the halogenolysis of Sn_2Me_6 was studied:

$Sn_2Me_6 + Hal_2 \longrightarrow 2Me_3SnHal$;

$\Delta H=(-70{,}24\pm0{,}5)$ kcal/mol for Br_2; $\Delta H=(-44{,}02\pm0{,}7)$ kcal/mol for I_2 [109].

$Et_3GeSnMe_3$ [42], Sn_2Et_6 [27,54], Sn_2Bu_6 [54,210], $Sn_2(i\text{-}Bu)_6$, Sn_2Ph_6, Ph_3SnSnR_3, $Et_3SnSn(i\text{-}Bu)_3$ and $Me_3SnSnEt_2(CH_2)_5SnEt_2SnMe_3$ [54], $(i\text{-}Bu_2SnCl)_2$ [27], $(Ph_2SnCl)_2$ [230], $(Bu_2SnF)_2$ [288], Me_5Sn_2Br [278], Et_5Sn_2Br [278,314] and Ph_3GePbR_3 [41], can be qualitatively titrated with halogens. Unambiguous reactions of OBMC with halogens were suggested for determining quantitatively Sn_2Et_6 (with I_2) [81,82], and Sn_2Et_6, Sn_2Pr_6, Sn_2Bu_6 and $Me_3SnSnPh_3$ (with Br_2) [82]. The method allows one to determine quantitatively Sn_2Me_6 in the presence of Me_4Sn (bromination) 84 , and Pb_2Et_6 in Et_4Pb (iodination) [85,279].

Iodine was found to be unreactive towards Si_2Ar_6 [61,63,78], $Ph_3SiGePh_3$ [65] and Ge_2Ph_6 [66], perhaps because of the steric hindrance. Bromolysis of Si_2Ph_6 gives Ph_3SiBr [67]; Ge_3Ph_6 is brominated (no faster than Ph_4Ge), affording Ph_3GeBr [62]. $Ge_2(C_6F_5)_6$ reacts with I_2 in the presence of $ZnCl_2$ only to produce $(C_6F_5)_3GeCl$ and ZnI_2 [201]. Iodolysis of $Ph_3GeSnPh_3$ gives Ph_3GeI [71]. Iodolysis of the Sn-Sn bonds in organoditins with the bulky substituents - $Sn_2Bu^t_6$ [72], $Sn_2(CH_2Bu^t)_6$ [73], $Sn_2(9\text{-}Phen)_6$ [169] - takes place at slow rates. On the other hand, iodolysis of $(Bu^t_2SnPh)_2$ [72], $Sn_2(CH_2CH_2Bu^t)_6$ [74], and $Sn_2(2,4,6\text{-}Me_3C_6H_2)_6$ [53], as well as iodolysis and bromolysis of $Sn_2(2\text{-}PhC_6H_4)_6$ [49] and $Pb_2(CH_2Bu^t)_6$ [75,76] proceed readily to yield R_3MHal.

For early investigations of Pb_2R_6 halogenolysis see [10]. The reactions of Pb_2Bu_6 with either Br_2 or I_2 (in Et_2O, at -60°C) were found to give Bu_3PbHal, while at -10°C - in Bu_2PbHal_2, as a result of a subsequent halogenolysis of Bu_3PbHal. Halogenolysis of Pb_2Ph_6 proceeds in a more complicated way; Ph_4Pb and PbI_2, along with the Ph_3PbI, are the main products. The yield of Ph_3PbI was raised to 90% by adding KI. The presence of two reaction pathways was assumed:

$2Ph_3PbI \longleftarrow Pb_2Ph_6 + I_2 \longrightarrow PhI + Ph_5Pb_2I$;

the Ph_4Pb and PbI_2 formation is the result of disproportionation of Ph_5Pb_2I [91]. The Pb - C bond breaking in Pb_2Ar_6 is the only known example of M - C bond halogenolysis upon interaction of OBMC with halogens; normally, the electrophilic halogen molecule affects the M-M bond.

The Ge-Ge-bond is broken in bromolysis reactions of digermacycloalkanes with the following order of reactivity:

$$Ge_2Et_6 \ll Et_2\overline{Ge(CH_2)_4Ge}Et_2 < Et_2\overline{Ge(CH_2)_3Ge}Et_2$$

which is accounted for by the strain of the Ge-Ge bond within a ring [197]. Bromine and iodine split the Si-Si-bond in $RMe\overline{SiSiMe_2CH_2CH_2C}H_2$ (R=Pr,i-Pr) [137]. Halogenolysis of $Me_2\overline{SiSiMe_2CH_2C}H_2$ results in $HalMe_2SiCH_2CH_2SiMe_2Hal$ (Hal=Cl, Br); the chlorination at room temperature proceeds with inflammation, and only at low temperatures was it possible to isolate the final product in 85% yield [99]. In the same manner $HalSiMe_2CMe_2CMe_2SiMe_2Hal$(Hal=Cl,Br) were obtained from $Me_2\overline{SiSiMe_2CMe_2C}Me_2$ [271]. Bromolysis of the Si-Si bond in 1,2-bis-(trimethylsilyl)-3,3,4,4-tetramethyl-3,4-disilacyclobutene [98] and 9,10-dimethyl-9,10-disiladecalin [100] was described. Reaction of $Me_2\overline{SiSiMe_2CH_2CH{=}CHC}H_2$ with Br_2 leads to $CH_2{=}CHCH{=}CHSiMe_2SiMe_2Br$ and $(Me_2SiBr)_2$ without bromolysis of the Si-Si-bond [101].

Si_2Me_6 reacts readily with Cl_2 in the dark (in gas phase) to form a single product:

$$Si_2Me_6 + Cl_2 \longrightarrow 2Me_3SiCl^{*}.$$

The "hot" molecules of Me_3SiCl^{*} formed via the exothermic reaction loose their energy upon colliding with the CH_4 molecules, which are added to the reaction mixture [110]. Organic halodisilanes react with halogens only slowly or do not react at all [103-105].

Reactions of a series of $MM'Me_6$ (M,M'=Si,Ge,Sn) with halogens were studied [111]. Reactions of Me_3MSnMe_3(M=Si,Ge) with ICl produce Me_3SnI and Me_3MCl. The product composition is controlled by the complementary influence of the secondary processes of interhalogen displacement upon the main process of the M-M' bond halogenolysis; this kinetic control is determined by Pearson's HSAB relation [112]. The OBMC reactivity in reaction with ICl follows the sequence

$$Me_3SnGeMe_3 > Me_3SnSiMe_3 \gg Me_3SiGeMe_3 > Ge_2Me_6 > Si_2Me_6.$$

The halogen reactivity has the following order: $Br_2 > ICl > I_2$.

The reactions of a series of organodisilanes with halogens in

CCl_4 solution were studied [113]. The kinetic and activation parameters for the bimolecular processes are presented in the Table. The mechanism suggested involves a four-center cyclic transition state. The data in the Table show that the substitution of alkyl groups by Cl decelerates drastically the halogenolysis rate. The sequence of halogen reactivity is the usual one: $Cl_2 > Br_2 \gg I_2$. For bromolysis of $(Me_2SiPh)_2$ in CCl_4 the ionic mechanism is suggested (but not established) to involve the formation of Me_2PhSi^+, $Me_2PhSiBr$ and Br^- [115]. For iodination of Sn_2Ph_6 in cyclohexane a molecular process is suggested, involving a 4-membered cyclic transition state [114].

The kinetics of Sn_2R_6 iodolysis was investigated and discussed [117,120]; the reactivity sequence is as follows [120]:

$$Sn_2Me_6 < Sn_2Et_6 > \begin{matrix} Sn_2Pr_6 \\ Sn_2Bu_6 \end{matrix} \gg \begin{matrix} Me_3SnSnPh_3 \\ Et_3SnSnPh_3 \end{matrix} > Sn_2Ph_6 > Sn_2(4\text{-}MeC_6H_4)_6 .$$

Iodolysis of a wide range of OBMC was also investigated [118]. The silicon- and germanium-containing OBMC were shown to react with iodine with measurable rates in PhCl (see Table). In the case of tin-containing OBMC which react very readily, I^- was added. The authors of [118] discussed the influence of substituents upon the rate of OBMC iodolysis (steric and inductive effects). As can be seen from the data presented in [118,120], the reactivity of Sn_2R_6, which has approximately the same order of magnitude for the whole series of Sn_2Alk_6, diminishes on going over to $Alk_3SnSnAr_3$, and, especially, to Sn_2Ar_6. Carboxylates $(RCO_2SnPh_2)_2$ are split by iodine to give RCO_2SnPh_2I. The reaction rate reduces with increasing electronegativity of the R group: $CF_3 < CCl_3 < CHCl_2 < CH_2Cl < CH_3$. It was pointed out that Sn_2Ph_6 is iodinated under the same conditions much more readily than the carboxylates [121].

The investigation of complexation and chemical reactions in the systems Si_2Alk_6-Hal_2 was carried out in 1979-1982 [160-162]. It was established for the first time that Si_2Me_6 and Si_2Et_6 do form donor-acceptor complexes (DAC) with Br_2 and I_2 (e.g., in CCl_4: $Si_2Me_6 \cdot Br_2$ λ^{CTB}_{max} = 295 mm; $Si_2Me_6 \cdot I_2$ - 297 nm; $Si_2Et_6 \cdot I_2$ - 300 nm). Similar DAC with halogens are formed also with Alk_4Sn [164,165], Et_4Ge [160,162,165], Me_4Si [160-162] and Et_4Si [160-162,165], the λ max values for Alk_4Si being shifted to short

Table

OBMC	Hal_2	Solvent	k_2 (T^oC) l/mol.s	E_{act} kcal/mol	ΔS≠ e.u.	ref.
Si_2Me_6	Br_2	CCl_4	2,5 (23,5°)	10,2	24,6	161,162
			1,26 (20°)	-	-	203
		$(ClCH_2)_2$	8,1 (23,5°)	9,2	25,5	161,162
$(Et_2SiMe)_2$		CCl_4	0,334 (20°)	5,2	43,1	113
Si_2Et_6		CCl_4	0,24 (23,5°)	10,4	28,7	161,162
		$(ClCH_2)_2$	0,25 (23,5°)	8,7	33,8	161,162
$(Me_2SiPh)_2$		CCl_4	21,00 (25°)	10,52	25,40	115
			1/mol·min			
Me_5Si_2Cl		CCl_4	0,058 (20°)	9,2	33,1	113
$(Me_2SiCl)_2$		CCl_4	$3,00.10^{-3}$(20°)	11,9	29,1	113
Si_2Me_6	I_2	CCl_4	$3,34.10^{-4}$(20°)	10,5	39	113
		$(ClCH_2)_2$	$3,5.10^{-3}$(23,5°)	9,7	39,3	161,162
		C_6H_5Cl	$9,7.10^{-4}$(20°)	14,2	lgPZ=7,5	118
$(Et_2SiMe)_2$		CCl_4	$2,46.10^{-4}$(20°)	11,7	35	113
Si_2Et_6		C_6H_5Cl	$7,0.10^{-5}$(20°)	15,1	lgPZ=7,2	118
$PrSi_2Me_5$		CCl_4	$4,00.10^{-4}$(20°)	7,9	47	113
$Si_2(i\text{-}Pr)_6$		C_6H_5Cl	$< 10^{-5}$(40°)			118
Me_5Si_2Cl		CCl_4	7.10^{-5}(30°)			113
$(Me_2SiCl)_2$		CCl_4	very slow			113
Ge_2Me_6		C_6H_5Cl	0,183 (20°)			118
$Me_3GeGeEt_3$		C_6H_5Cl	$9,2.10^{-2}$(20°)	9,0	lgPZ=5,8	118
Ge_2Et_6		C_6H_5Cl	$6,35.10^{-2}$(20°)	9,7	lgPZ=6,0	118
$Et_3GeSnEt_3$		C_6H_5Cl	very fast			118

wave region compared to those for Si_2Alk_6. It appears that the electron-donor in the DAC $[Si_2Alk_6 \longrightarrow I_2]$ is the Si-Si bond, which has a low ionization potential (IP). A linear correlation between E_{CT}(=hc/λ) and IP of σ-donors was established [160,162].

The kinetic equation of halogenolysis: $W=k_2\,[Si_2R_6][Hal_2]$ - involves no third-order term. Radical inhibitors of various types show no effect upon the reaction rate; evidènce was suggested to favour the molecular pathway for the hexaalkyldisilanes' halogenolysis, involving no radical, or ionic intermediates [161,162].

The probable stereochemical results of the halogenolysis of M_2R_6 were also theoretically examined [162,163].

The kinetics of bromolysis of a series of Si_2R_6 in CS_2 solution was studied [116]. Stepwise replacement of methyl groups by phenyl groups reduces the reactivity of Si_2R_6. As one may expect, $4\text{-}FC_6H_4$-substituted disilanes reacted slower than their Ph-analogues.

SCF CNDO calculations have been published [170] for the reaction $Si_2H_6 + Cl_2 \longrightarrow 2SiH_3Cl$. Assuming a 4-membered planar symmetric cyclic transition state the E_{act} value was found to be 31.5 kcal/mol, which falls within the range of experimental E_{act} values for the Si_2R_6 halogenolysis reactions (see Table). To investigate the reactivity of Si-Si-bonds in chlorolysis, MO--analysis of Si_2Me_6 and permethylpolysilanes was carried out [151].

II. ACIDS

Electrophilic dealkylation (dearylation) is one of the powerful synthetic approaches in organo-silicon chemistry. The first important results in the field were reported by Kumada et al. They showed that the reaction of Si_2Me_6 and H_2SO_4 with subsequent treatment with NH_4F (NH_4Cl) gives Me_5Si_2X and $(Me_2SiX)_2$ [178]. In such a way $ClCH_2SiMe_2SiMe_2OSO_3H$ [232] and $ClCH_2SiMe_2SiMe_2Cl$ [86] were obtained from $ClCH_2Si_2Me_5$; $(Me_2GeCl)_2$ and $(Bu^tMeGeCl)_2$ from Ge_2Me_6 and $(Me_2GeBu^t_2)_2$ [105]. It was found that the Ph-group is cleaved from phenylmethyl disilanes: $Me_3SiSiMe(Ph)CH_2Br$ is transformed into $Me_3SiSiMe(Cl)CH_2Br$ and $PhMe_2SiSiMe_2CH_2Br$ into $ClMe_2SiSiMe_2CH_2Br$ [195]. $Me_3SiSiMeCl_2$ is obtained from $Me_3SiSiMePh_2$ under the action of H_2SO_4/NH_4Cl, HCl or $HCl/AlCl_3$ [192,215,297].

The protolysis of disilacycloalkanes was studied using the system H_2SO_4/NH_4HF_2 [188]. So, 5- and 6-membered rings react at the Si-Si bond only:

$$Me_2\overline{Si(CH_2)_nSi}Me_2 \longrightarrow FMe_2Si(CH_2)_nSiMe_2F \quad (n=3,4)$$

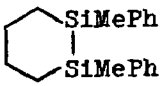
Protolysis of the 7-membered ring gives a mixture of products:

$$Me_2\overline{Si(CH_2)_5Si}Me_2 \longrightarrow C_5H_{11}SiMe_2SiMe_2F + Me_2\overline{Si(CH_2)_5Si}MeF +$$

$$+ FMe\overline{Si(CH_2)_2Si}MeF + C_5H_{11}(Me)SiFSiMe_2F + FMe_2Si(CH_2)_5SiMe_2F$$

At 17-18°C the first two compounds are the major products. At 35°C all the products are generated in approximately equal quantities, the total yield being 7%. These results are accounted for by the strain of the Si-Si-bond within 5- and 6-membered rings. The 7-membered ring lacks such a strain, that is why the electrophile attacks the Si-Si-bond, as in the case of Si_2Me_6, and the reaction with H_2SO_4 proceeds at the same rate as with Si_2Me_6. The strained 5- and 6-membered rings react with H_2SO_4 more readily; electrophiles attack the Si-Si-bond [188].

The phenyl-containing disilane I by similar treatment affords the difluoride II , whereas the subsequent treatment with NH_4Cl affords the dichloride III [186,190]. The last compound can also be obtained when I is treated with HCl in the presence of $AlCl_3$ [190]. Similarly, $PhMe\overline{Si(CH_2)_5Si}MePh$ reacts with H_2SO_4/NH_4HF_2 to give $FMe\overline{Si(CH_2)_5Si}MeF$. On the other hand, the compound IV is transformed into $(BuMeSiF)_2$ under the same conditions [64]. In this case the Si-Si-bond, which is not incorporated into the ring, is unaffected.



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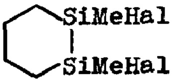
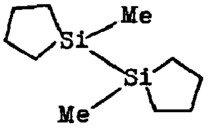


II, III



IV

Reactions of organodisilanes with hydrogen halides occur (in the absence of catalyst) only at high temperatures and result in Si-Si-bond breaking. Thus, Si_2Me_6 reacts with HCl at 350-400°C to yield Me_3SiCl and Me_3SiH; Me_5Si_2Cl yields (at 500°C) Me_3SiCl and Me_2SiHCl [64,206]. Reaction of the "disilane fraction" (containing mainly $(MeSiCl_2)_2$ and $Me_2SiClSiMeCl_2$) with HCl produces $MeSiCl_3$, Me_2SiCl_2 and $MeSiHCl_2$ [18]. Reaction of H_3PO_4 with the "disilane fraction" gave Me_2SiCl_2 and $MeSiCl_3$; the products of the reaction with $(NH_4)_3PO_4$ or $(NH_4)_2HPO_4$ are Me_2SiCl_2, $MeSiHCl_2$ and Me_2SiHCl [211].

In the presence of the catalysts $AlHal_3$, hydrogen halides dealkylate organodisilanes. For example, reaction of Si_2Me_6 with $HCl-AlCl_3$ at 20°C produces Me_5Si_2Cl; at 50-60°C - $(Me_2SiCl)_2$; at 90°C - $Me_3Si_2Cl_3$ [196]. Similarly, from the "disilane fraction" $(MeSiCl_2)_2$ can be obtained [212,213]; methylchlorodisilanes $Me_nSi_2Cl_{6-n}$ (n=3-5) and $(Me_2SiCl)_2$ yield $(MeSiCl_2)_2$ and $Me_3Si_2Cl_3$ respectively [213,214]. The loss of one or several Ph-groups was observed in the reactions of HHal (either in the presence or in the absence of $AlHal_3$) with the Ph-containing silicon and germanium OBMC [20,43,90,100,108,192,215-222,250]. The reaction of Ge_2Ph_6 with HCl leads to $(Ph_2GeCl)_2$ [220], but Ph_3GeCl was obtained in the presence of $AlCl_3$ [92].

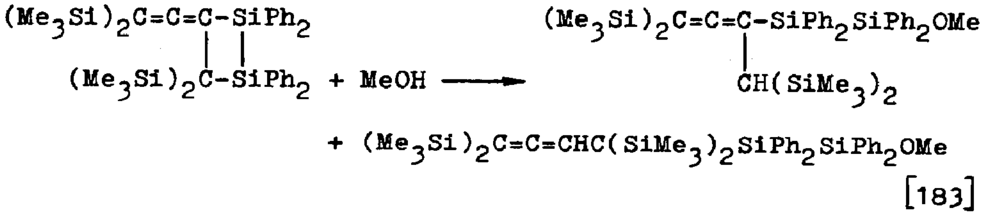
By the action of H_2SO_4 on $Me_5Si_2C(Me){=}CH_2$ the initially formed carbocation undergoes rearrangement:

$$Me_3Si - SiMe_2 - CMe_2^+ \longrightarrow Me_2Si^+ - CMe_2 - SiMe_3$$

The following products can be isolated: $Me_3SiCMe_2SiMe_2OH$ (after treating with H_2O), or a mixture of $Me_3SiCMe_2SiMe_2F$ and $Me_2C(SiMe_2F)_2$ (after treating with NH_4F). Similarly, protolysis of $[Me_2Si\underset{Me}{C}{=}CH_2]_2$ gave $Bu^tMeFSiCMe_2SiMe_2F$, $Me_2C(SiMe_2F)_2$ and propene; protolysis of $CH_2{=}C(Me)(SiMe_2)_3C(Me){=}CH_2$ gave $Me_2Si(CMe_2SiMe_2F)_2$ [196]. $Ph_3SiSiMe_2CPhBr_2$ When hydrolyzed gives rise to $Ph_3SiCPhBrSiMe_2OH$; in this latter case the Ph_3Si group migrates within the intermediate cation $Ph_3SiSiMe_2CPhBr^+$ [149].

In a number of cases the Si-Si- and Si-C-bonds take no part in the reactions of organodisilanes with acids. Thus $(Me_2SiCH_2OMe)_2$ reacts with KI/H_3PO_4 to give $MeOCH_2(SiMe_2)_2CH_2I$ and $(Me_2SiCH_2I)_2$ [195]; protodemercuration of $RMe_2SiSiMe_2CH_2HgR'$ under the action of HCl has been studied [187]. Reaction of H_2SO_4 with $(PhEtPrSi)_2$ yields PhH; $(PhCH_2SiEtPr)_2$ is transformed into $(EtPrSiCH_2C_6H_4SO_3H)_2$ [102].

Protolysis of the disilacyclohexene $Me_2\overline{SiSiMe_2CH_2CH{=}CHC}H_2$ proceeds with ring cleavage to give $CH_2{=}CHCH_2CH_2SiMe_2SiMe_2X$ (X=Br, HCO_2, AcO, $EtCO_2$) [101,200]. Reaction of $F_2\overline{SiSiF_2CH_2CH{=}CHC}H_2$ with HF yielded cis-2-butene [204]. The strained 3- and 4-membered cyclic disilanes are generally reactive even towards weak acids. Thus $Me_2\overline{SiSiMe_2CH_2C}H_2$ reacts with HCl and HBr giving $Me_2SiHCH_2CH_2SiMe_2X$, while the reaction with MeOH produces $(MeOSiMe_2CH_2)_2$ [99]. Protolysis of the Si-Si-bond in $Me_2\overline{SiSiMe_2CMe_2C}Me_2$ was also reported [271]. Other examples are presented below:



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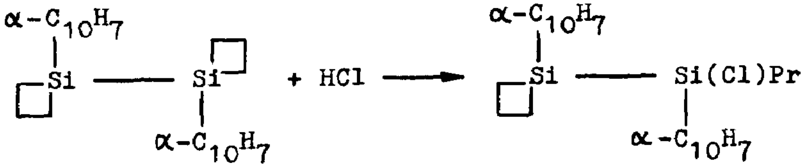

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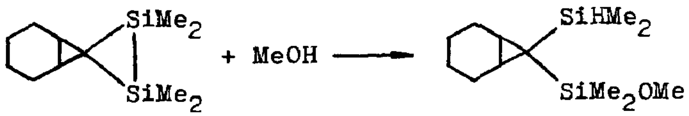
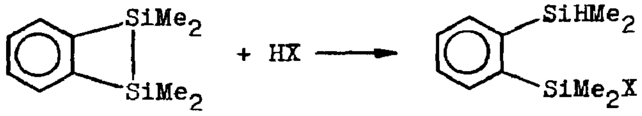
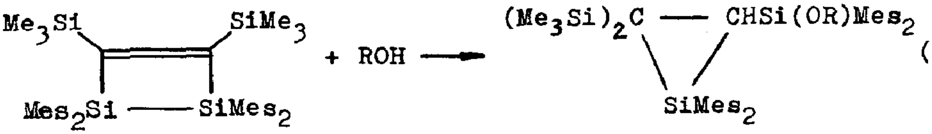


[185]



(X=Cl,OEt) [173]

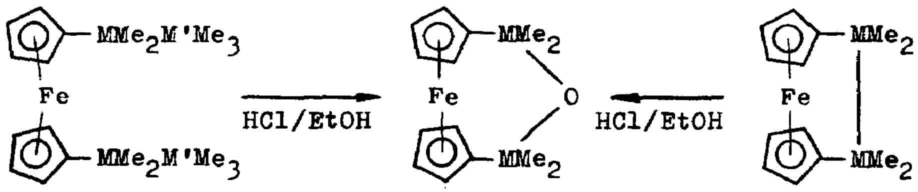


(R=H,Me)

[158]

Protolysis reactions of 1-silylsilacyclopropanes and 1-silylsilacyclopropenes are described in refs [23,180, 182,184,293,294]. It was noted, however, that the sterically crowded 1,1,2,2-tetramesityl-phenyltrimethylsilyl- and -bis(trimethylsilyl)-exomethylene-1,2-disilacyclopropanes did not react with alcohols [22].

Protolysis of ferrocenyl-substituted OBMC of silicon and germanium proceeds under mild conditions and leads to the breaking of both M-M' and M-C bonds. At low HCl concentrations the main reaction products are disiloxanes (digermanoxanes), e.g. [191, 192]:



$$CpFeC_5H_4SiMe_2MMe_3 + HCl/EtOH \longrightarrow CpFeC_5H_4SiMe_2OEt + Me_3MOEt$$

$$CpFeC_5H_4GeMe_2MMe_3 + HCl/EtOH \longrightarrow (CpFeC_5H_4GeMe_2)_2O \quad (M,M'=Si,Ge)$$

The reaction seems to proceed through the formation of the ferricinium ion.

Si_2Ph_6, $Ph_3SiGePh_3$ And Ge_2Ph_6 were shown not to react with glacial HOAc at 140°C even in the presence of $AlCl_3$, but Ph_3MSnPh_3 (M=Si,Ge) reacted with the refluxing glacial HOAc to give $(AcO)_3MSn(OAc)_3$ (the intermediate $Ph_3GeSn(OAc)_3$ was also isolated) [40]. Similarly, $Sn_2(OAc)_6$ was obtained by acetolysis of Sn_2Ph_6 [58]. All the acetoxyl derivatives prepared were quite stable. Strong carboxylic acids split Ge_2Ph_6 to form either $RCO_2Ge_2Ph_5$ or $(RCO_2GePh_2)_2$ (R=CCl_3, CF_3, but not CH_3, CH_2Cl) [92,224]. In contrast to Ge_2Ph_6 the C_6F_5-containing digermanes react readily even with weak acids with the Ge-Ge-bond breaking [201]:

$$(C_6F_5)_3GeGeR_3 + HX \longrightarrow (C_6F_5)_3GeH + R_3GeX (R{=}C_6F_5, Et)$$

It was established [111] that $Me_3SnGeMe_3$ and $Me_3SnSiMe_3$ react with HCl (the first compound reacting at higher rates than the second one):

$$Me_3SnSiMe_3 + HCl \longrightarrow Me_3SnCl + Me_3SiCl + H_2$$

$$Me_3SnGeMe_3 + HCl \longrightarrow Me_3GeSnMe_2Cl + Me_3SnCl + Me_3GeCl + H_2$$

Si_2Me_6, $Me_3SiGeMe_3$ And Ge_2Me_6 undergo no cleavage when treated with HCl. The reaction of Sn_2Et_6 with HCl was carried out as early as in 1870, and gave Et_2SnCl_2, C_2H_6 and H_2 [225]. Sn_2Et_6 Does not react with HOAc (or $PhCO_2H$) at 80°C, but at 135°C Et_3SnOAc, $Et_2Sn(OAc)_2$, C_2H_6 and H_2 can be obtained [227]. Reaction of Sn_2Et_6 and $ClCH_2CO_2H$ produces Et_2SnCl_2, C_2H_6, C_4H_{10} and CO_2 [228]. In MeOH solution Sn_2Me_6 reacts with HCl [226] and HBr [42] to form Me_3SnHal.

Sn_2Ph_6 Was reported not to react with H_2SO_4 (in THF solution), but it does react with HCl to give Ph_3SnCl and H_2 [229]. On the other hand, reaction between Sn_2Ph_6 and HCl (in dry PhH) gave $(Ph_2SnCl)_2$ [230]. The compounds of $(RCO_2SnMe_2)_2$ type were synthesized with good yields from Sn_2Me_6 and RCO_2H (with R=CHF_2, CF_3, CH_2Cl, $CHCl_2$, CCl_3, but not CH_3, CH_2I, CBr_3) at low temperatures [175,231]. Highly sterically crowded $Sn_2[CH(SiMe_3)_2]_6$ is cleaved by water to give $[(Me_3Si)_2CH]_3SnOH$ [199].

Protolysis of Me_3MSnMe_3 (M=Si,Ge,Sn) was investigated in more detail [317]. Me_3SnCl Was shown to be the only product in the reaction of Sn_2Me_6 with HCl (in MeOH solution), while mixed OBMC react in two ways:

$$\mathrm{Me_3MSnMe_2Cl \longleftarrow Me_3MSnMe_3 + HCl \longrightarrow Me_3MCl + Me_3SnCl}$$

$$\mathrm{Me_3MSnMe_2Cl \longrightarrow Me_3MCl + Me_2Sn}$$

$$\mathrm{Me_2Sn + 2HCl \longrightarrow Me_2SnCl_2}$$

On the other hand, CF_3CO_2H leads to $CF_3CO_2SnMe_2MMe_3$ only (by NMR-spectroscopy), but attempted isolation gave $CF_3CO_2MMe_3$.

The protolysis reactions of Pb_2R_6 are characterized by the diversity of products; see [10]. Pb_2Ph_6 And HCl react at low temperatures to form merely Ph_3PbCl and $PbCl_2$; this can be accounted for by one of the two reaction pathways [91]:

$$\mathrm{Pb_2Ph_6 + HCl \longrightarrow Ph_5Pb_2Cl \longrightarrow Ph_3PbCl + Ph_2Pb}$$

$$\mathrm{Ph_2Pb + 2HCl \longrightarrow PbCl_2}$$

$$\mathrm{or\ Pb_2Ph_6 + 3HCl \longrightarrow Ph_2ClPbPbPhCl_2 \longrightarrow Ph_3PbCl + PbCl_2}$$

Acetolysis of Pb_2Ph_6 (in refluxing benzene or n-heptane) gave Ph_4Pb, Ph_3PbOAc, $Pb(OAc)_2$ and PhH; use of boiling HOAc results in $Ph_2Pb(OAc)_2$ and $Pb(OAc)_2$ [241]. MeC(O)SH Reacts similarly. Aqueous solutions of HOAc or HCOOH were employed to purify Et_4Pb from Pb_2Et_6 [236]. Ar_2PbX_2 Derivatives were obtained in the reaction of $Pb_2(4\text{-}MeC_6H_4)_6$ with nitrous and iso-butanoic acids [242]. Ph_2Ph_6 And maleic acid afforded Ph_2Pb-maleate [91].

The following pathway was proposed [243] for Pb_2Me_6 methanolysis:

$$\mathrm{Pb_2Me_6 + MeOH \longrightarrow Me_5Pb_2OMe + MeH}$$

$$\mathrm{Me_5Pb_2OMe \longrightarrow Me_3PbOMe + Me_2Pb}$$

$$\mathrm{Me_2Pb + 2MeOH \longrightarrow Pb(OMe)_2 + 2MeH}$$

$$\underline{\mathrm{Pb_2Me_6\ +}}\ \mathrm{2Me_3PbOMe \longrightarrow 3Me_4Pb + Pb(OMe)_2}$$

$$\mathrm{Pb_2Me_6 + 2MeOH \longrightarrow Me_4Pb + Pb(OMe)_2 + 2MeH}$$

Acetolysis of Pb_2Ar_6 gives rise to Ar_3PbOAc, $Pb(OAc)_2$ and ArH [245]. The kinetic equation of the reaction is: $W=k[Pb_2Ar_6][HOAc]^n$ ($n=3\div3{,}5$). The correlation was established between the acetolysis rate and the σ-values of the Ar-groups (except for 4-$MeOC_6H_4$); $\rho = -2{,}3$. The formation of 1,1,2-$Ar_3Pb_2(OAc)_3$ as an isolated intermediate [245] was, however, experimentally refuted later [93]. The kinetics of the reactions between Pb_2Ar_6 and HCl were studied in [246]. The reactivity of five Pb_2Ar_6 compounds was shown to satisfy the Yukawa-Tsuno equation [247]: $\lg k/k_0 = \rho[\sigma + r(\sigma^{+} - \sigma)]$, with $\rho = -2{,}9$; $r = 0{,}6$. The rate-determining step for the reaction is the electrophilic replacement at the carbon atom (protodeplumbylation) by undissociated HCl.

III. LEWIS ACIDS

Reactions of OBMC with Lewis acids have been widely and thoroughly studied. Kumada et al. [250] have carried out the following reactions:

$$Si_2Me_6 + Me_3SiX \longrightarrow Me_5Si_2X + Me_4Si (X=Cl, I)$$

$$Si_2Me_6 + 2Me_3SiX \longrightarrow (Me_2SiX)_2 + 2Me_4Si (X=Cl, Br)$$

$$Si_2Me_6 + (Me_2SiCl)_2 \xrightleftharpoons[AlCl_3]{} 2Me_5Si_2Cl$$

The equilibrium is considerably shifted to the right-hand side (K_e = 82,6), which makes it possible to use the reaction between Si_2Me_6 and $(Me_2SiCl)_2$ for the synthesis of Me_5Si_2Cl [251]. Si_2Me_6 On heating in the presence of $AlCl_3$ reacts with either Me_2SiCl_2 [252], or $MeSiHCl_2$ [253], or the "disilane fraction" [159] to form Me_2SiCl_2. Reaction of Si_2Me_6 with Si_2Cl_6 leads to Me_2SiCl_2, Me_3SiCl, $Me_2ClSiSiMeCl_2$, $(Me_2SiCl)_2$ and $(MeSiCl_2)_2$ [119].

The data of [254] show that in the absence of a solvent the reaction of Si_2Me_6 with MCl_4 (M=Te, Ti, Se, Ge, Sn), as well as with PCl_5, $FeCl_3$ and $SbCl_5$ occurs with Si-Si-bond breaking. It should be noted, however, that the Si-Si-bond breaking in Si_2Me_6 under the action of such reagents as $SbCl_5$, $GeCl_4$ and $SnHal_4$, is somewhat unexpected, since these reagents usually break the C-M-bonds in the silicon and germanium OBMC. For instance, Si_2Me_6 and $SbCl_5$ react in CH_2Cl_2 solution to form Me_5Si_2Cl [255]. It was pointed out that a mixture of Si_2Me_6 with $AlCl_3$ and $TiCl_4$ ($TiCl_3$, VCl_4) catalyzes ethylene polymerization [256]. The reaction between Si_2Me_6 and SF_6 afforded $Me_2Si\langle{}^{S}_{S}\rangle SiMe_2$ [257]. The compounds of the type  $\underset{Me}{R_3MSi}$ ($R_3M=Ph_3Si$, Ph_3Ge, Me_3Sn) readily reduce an alcoholic solution of $AgNO_3$ [258]. The reaction of $Me_3SiSi(Ph)CH_2CHCH_2OEt$ with $Et_2O.BF_3$ leads to $Me_3SiSiPh(F)CH_2CH{=}CH_2$ without Si-Si-bond splitting [182].

At elevated temperatures organodisilanes react with $CuCl_2$ to form the corresponding compounds R_3SiCl [261,262]; see also [131].

$Hg(OAc)_2$ Reacts (on heating) with Si_2Me_6 and $Me_3SiSiPh_3$, but not with Si_2Ph_6, to form R_3SiOAc and Hg. Si_2Me_6 And $(MeSiEt_2)_2$ react with $NiCl_2$ $(NiBr_2)$ to give Alk_3SiHal. Heating of $Me_3SiSiPh_3$ with $AgNO_3$ resulted in the formation of silver, NO and siloxanes [261]. Reaction between Si_2Ph_6 and $AgNO_3$ requires a temperature of 230°C and leads to $(Ph_3Si)_2O$ and nitrogen axides; it is to be noted that Ph_4Si does not react under these conditions [61]. Reaction between Si_2Me_6 and Ge_2Me_6 with $Hg(OAc)_2$ (in the MeOH solution) lead to $(Me_3M)_2O$ and $Hg_2(OAc)_2$; under the reaction conditions the initially formed Me_3MOAc is hydrolyzed into $(Me_3M)_2O$. Sn_2Me_6 Gives Me_3SnOAc and $Hg_2(OAc)_2$ [153]. Ge_2Ph_6 Reduces $AgNO_3$ to Ag [19].

WCl_6 And $MoCl_5$ were found to break the M-M-bonds in OBMC:

$$M_2R_6 + WCl_6(MoCl_5) \longrightarrow 2R_3MCl + WCl_4(MoCl_3) (M=Si,Ge,Sn;R=Me,Pr)$$

The reactivity sequence is as follows: $Sn \gg Ge > Si$. Me_5Si_2Cl Reacts more slowly than Si_2Me_6, but Me_5Si_2Ph reacts rapidly, the Si-Si- and Si-Ph-bonds being broken. Compounds with M-W bonds are possible intermediates in the reactions. A linear correlation was established between the rates of cleavage of unbranched polysilanes Si_nMe_{2n+2} (n=2,3,4,6) by WCl_6 (as well as of Ge_2Me_6) and the first IP of the donor organoelements [130,265]. The reaction mixture of Sn_2Bu_6 and WCl_6 was found to catalyze cyclopentene polymerization, but the yield of linear polymer $(C_5H_8)_n$ is lower than in the case of catalysis with the mixture (Bu_4Sn + + WCl_6) [172].

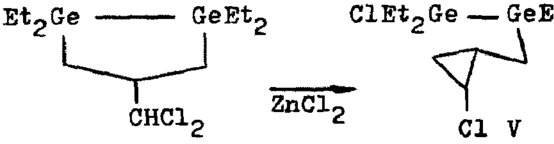
Kumada et al. have found the halogenomethyldisilane rearrangement catalyzed by $AlHal_3$. Thus $Me_5Si_2CH_2Cl$, when treated with $AlCl_3$, is rearranged into $Me_3SiCH_2SiMe_2Cl$, and $ClCH_2(SiMe_2)_2Cl$ into $CH_2(SiMe_2Cl)_2$ [86]. It is supposed that within the cation formed under the action of $AlCl_3$, the Me_3Si-group migrates, e.g.:

$$Me_3Si - SiMe_2 - CH_2^+ \longrightarrow Me_2Si^+ - CH_2 - SiMe_3$$

(see also Section II). Similarly, $Me_5Si_2CHCl_2$ when treated with $AlCl_3$ at 70-80°C is transformed into $Me_3SiCHClSiMe_2Cl$: at 140--150°C $MeCH(SiMe_2Cl)_2$ is formed (as a result of the subsequent Me-group migration) [107]; see also [108]. An analogous rearrangement takes place at -60° in the following reaction [195]:

$Me_5Si_2CH_2OMe + BCl_3 \longrightarrow Me_3SiCH_2SiMe_2Cl + MeOBCl_2$

A number of ferrocenyl-containing OBMCs of silicon and germanium were oxidized (in MeOH solution) by dissolved oxygen in the presence of an Fe III catalyst to give the corresponding disiloxanes, or digermanoxanes. In the absence of O_2 the stoichiometric quantity of Fe III is required. The proposed reaction mechanism involves the M-M-bond breaking within the ferricinium salt [194]. In the presence of catalytic quantities of $AlCl_3$ at 235°C Si_2Et_6 disproportionates forming Si^0 and Et_4Si [267,268]. At 200° in the presence of $AlCl_3$, or $AlBr_3$, Ge_2Et_6 disproportionates forming Et_4Ge, $(Et_2Ge)_n$ and $(Et_2Ge)_n$ [269]. The following reaction was carried out:



V

$+ (Et_2GeCl)_2 + CH_2{=}CHCH{=}CH_2$

The last two products are probably formed from V [262].

The reactions between Ge_2Alk_6 and MCl_4 have been studied [79, 80,273-276]. Thus Ge_2Et_6 at 200°C reacts with MCl_4 (M=C,Si,Ge, Sn) to give Et_5Ge_2Cl and (or) $(Et_2GeCl)_2$; Ge_2Bu_6 and $GeCl_4$ led to Bu_5Ge_2Cl. Ge_2Et_6 Reacts readily with $SnCl_4$ to form 100% of Et_5Ge_2Cl; by the reaction with two moles of $GeCl_4$, $(Et_2GeCl)_2$ was obtained. The regularities established are in good agreement with the electrophilic dealkylation rules exemplified earlier for Alk_4M. The following reactions are characterized by high selectivity:

$Me_3SiGeEt_3 + SnCl_4 \longrightarrow Me_3SiGeEt_2Cl + EtSnCl_3$

$Me_3GeGeEt_3 + SnCl_4 \longrightarrow Me_2ClGeGeEt_3 + MeSnCl_3$

$Et_5Ge_2Bu + SnCl_4 \longrightarrow Et_3GeGeEtBuCl + Et_2ClGeGeEt_2Bu + EtSnCl_3$

Me_5Ge_2Cl [29,80,89,207], $(Me_2GeCl)_2$ [207] and Pr_5Ge_2Cl [79] were also synthesized. Ge_2Ph_6 Was converted into Ph_3GeCl in the reaction with $GeCl_4/AlCl_3$ or $SnCl_4$ [92].

Razuvaev et al. [201,205,277] have studied the reactions between C_6F_5-substituted digermanes and distannanes, and a series of Lewis acids. It was established for example that Ge_2R_6 (in this paragraph $R{=}C_6F_5$) reacts with $HgCl_2$ or $CuCl_2$ to form R_3GeCl

and M_2Cl_2. The effect of EtHgCl upon Ge_2R_6 resulted in R_3GeCl and $R_3GeHgEt$. The following reactions were also carried out:

$$R_3GeGeEt_3 + X_3MHal \longrightarrow R_3GeMX_3 + Et_3GeHal$$

$$(X_3MHal{=}R_3GeBr, Et_3SnCl, \text{but not } R_3SiBr,\ R_3SnBr)$$

$$R_3MSnEt_3 + R_3M'Br \longrightarrow R_3MM'R_3 + Et_3SnBr\ (M,M'{=}Ge,Sn)$$

$$R_2Ge(H)SnEt_3 + R_2GeHBr \longrightarrow (R_2GeH)_2 + Et_3SnBr$$

$$Sn_2Et_6 + 2R_3SnBr \longrightarrow Sn_2R_6 + 2Et_3SnBr$$

The last reaction was represented as involving $R_3SnSnEt_3$ as an intermediate. $R_3SnSnEt_3$ And $HgCl_2$ react to give Sn_2R_6, Et_3SnCl and Hg^o; R_3SnCl, originating from the unstable $R_3SnHgCl$, is supposed to react further with the initial distannane to form Sn_2R_6. Reactions between $GeCl_4$ and Ge_2R_6 (or $R_3GeGeEt_3$) produce $R_3GeGeCl_3$ capable (at 100°C) of disproportionating with the formation of R_3GeCl and $(GeCl_2)_n$. Ge_2R_6 And $SnCl_4$ led to R_3GeCl, which was tentatively ascribed to the decomposition of the originally formed $R_3GeSnCl_3$. Thus the reactions of C_6H_5-containing OBMC with electrophiles proceed with M-M-bond breaking; the product composition is determined by the stability of the intermediate organobimetallic compound.

Organic distannanes and diplumbanes react readily with $AgNO_3$, reducing the latter to metallic silver [48-50,229,230,279-281, 286,288]. It was established [285] that Pb_2Ph_6 reacts with $AgNO_3$ to form the green-coloured complex $[Ag_2(Pb_2Ph_6)]^{+2}$, the latter being stable at low temperatures. The complex decomposes quantitatively into Ag^o and Ph_3PbNO_3. Silvermetric titration with Sn_2R_6 was employed to determine the distannane concentration in solution [82]. The kinetics of the reactions between Sn_2R_6 and Ag^+ (in the presence of pyridines) were investigated [284]; the reactivity follows the order

$$\begin{array}{l} Me_3SnSnPh_3 \\ Sn_2Me_6 \end{array} \gg Sn_2Et_6 > Et_3SnSnPh_3 > \begin{array}{l} Sn_2Pr_6 \\ Sn\ Bu_6 \end{array} > Sn_2Ph_6 > Sn_2(i\text{-}Pr)_6$$

The difference in oxidation rates made possible the separate silvermetric titration of the distannane pairs:

Sn_2Me_6 + Sn_2Et_6; Sn_2Et_6 + Sn_2Bu_6; Sn_2Me_6 + Sn_2Bu_6; $Me_3SnSnPh_3$ + + Sn_2Ph_6 [82,283].

Sn_2Alk_6 Reduces $BiBr_3$ to Bi^o [295]. Reaction between Sn_2Me_6 and $AuCl_3$ led to Me_3SnCl and Me_2SnCl_2 [226]. Sn_2Ph_6 Is transformed into Ph_3SnCl when affected by $CuCl_2$, $HgCl_2$, $SnCl_4$, $FeCl_3$ [229]. Sn_2R_6 And $HgCl_2$ give R_3SnCl [42,49,285,295]. Tin and lead OBMC were observed to be reduced to R_3M^+ by $Hg_2(NO_3)_2$ [308]. Reaction between Sn_2Et_6 and PhHgCl (at 150-160°C) produced $PhSnEt_3$ (38%), Et_3SnCl and Hg^o [296]. Sn_2Me_6 Reacts with $Hg(CF_3)_2$ to give Me_3SnCF_3, C_3F_6 and Me_4Sn. Si_2Me_6, Ge_2Ph_6 And Sn_2Ph_6 do not react with $Hg(CF_3)_2$; in reaction with Pb_2Ph_6 it has been possible to identify $PhHgCF_3$ [25].

Reactions of Sn_2R_6 with mercury salts were thoroughly studied [300]. The following schemes were proposed:

$$Sn_2Me_6 + HgCl_2 \longrightarrow Me_3SnCl + Me_3SnHgCl$$

$$Me_3SnHgCl \longrightarrow Me_3SnCl + Hg^o$$

$$Sn_2Me_6 + RHgX \longrightarrow Me_3SnX + Me_3SnHgR \; (\longrightarrow Me_3SnR + Hg^o)$$

$$Me_3SnHgR + RHgX \longrightarrow Me_3SnX + R_2Hg + Hg^o$$

Treatment of Pb_2Me_6 with MeHgCl resulted in the formation of Me_4Pb, Hg^o, $PbCl_2$ and Me_2Hg (in case of CD_3HgCl, CD_3HgCH_3 is obtained). The reactions are considered to involve electrophilic atack on both the Pb-Pb-bond and the Pb-C-bond [301]. $Pb_2(c\text{-}C_6H_{11})_6$ And $FeCl_3$ led to $(c\text{-}C_6H_{11})_3$ PbCl and $FeCl_2$ [289]. $Pb_2(2,6\text{-}Me_2C_6H_3)_6$ And $TlCl_3$ produced Ar_2PbCl_2 and TlCl [287]. Reactions of Pb_2R_6 (where R=Me,Ph,4-MeC_6H_4) with $TeCl_4$ give R_2TeCl_2, R_2PbCl_2 and $PbCl_2$; Pb_2Ph_6 and a series of $ArTeCl_3$ produced $PhArTeCl_2$, Ph_2TeCl_2 and $PbCl_2$ [21]. Pb_2Ph_6 And Ar_3SbX_2(X=Cl,Br,NCS) were found to react with the formation of Ph_4Pb, Ph_2PbX_2 and Ar_3Sb [290].

The reaction of Pb_2Ph_6 with $HgCl_2$ and $Hg(OAc)_2$ gives Ph_3PbX, Ph_2PbX_2, PbX_2, and PhHgX. Both Ph_4Pb and Ph_3PbCl were observed to react 40-50 times slower than Pb_2Ph_6. The proposed reaction scheme involves no initial Pb-Pb-bond cleavage:

$$Pb_2Ph_6 + HgX_2 \longrightarrow PhHgX + Ph_5Pb_2X$$

$$Ph_5Pb_2X \longrightarrow Ph_3PbX + Ph_2Pb$$

$$Ph_5Pb_2X + HgX_2 \longrightarrow (Ph_2PbX)_2 + PhHgX$$

$$(\mathrm{Ph_2PbX})_2 \longrightarrow \mathrm{Pb_2PbX_2} + \mathrm{Ph_2Pb}$$

$$\mathrm{Ph_2Pb} + 2\mathrm{HgX_2} \longrightarrow \mathrm{PbX_2} + 2\mathrm{PhHgX}$$

The reactivity of five Pb_2Ar_6 compounds satisfies the Hammett equation ($\rho = -4{,}5$) [302].

The following reactions were carried out [303-306]:

$$\mathrm{M_2Et_6} + \mathrm{Pb(OAc)_4} \longrightarrow 2\mathrm{Et_3MOAc} + \mathrm{Pb(OAc)_2} \quad (\mathrm{M{=}Sn,Pb})$$

$$\mathrm{Pb_2Bu_6} + \mathrm{Pb(OAc)_4} \longrightarrow 2\mathrm{Bu_3PbOAc} + \mathrm{Pb(OAc)_2}$$

$$\mathrm{Pb_2Ph_6} + 5\mathrm{Pb(OAc)_4} \longrightarrow 6\mathrm{PhPb(OAc)_3} + \mathrm{Pb(OAc)_2}$$

$Hg(OAc)_2$ Was the catalyst for the last reaction. $(NH_4)_2PbCl_6$ oxidizes M_2Ph_6 to form Ph_3MCl with reactivity sequence Pb > Sn > > Ge > Si (Si_2Ph_6 does not react). $Pb_2(n\text{-}C_{12}H_{25})_6$ Reacts with $(NH_4)_2PbCl_6$ to give R_3PbCl and R_2PbCl_2 [272].

It was previously pointed out that the reaction between Sn_2Ph_6 and $SnCl_4$ leads to Ph_3SnCl and $SnCl_2$ [229]. The reaction between Sn_2Bu_6 and $SnCl_4$ results in Bu_3SnCl, Bu_2SnCl_2 and $SnCl_2$; this fact was explained by the oxidative decomposition of Sn_2Bu_6 at the Sn-Sn-bond; Bu_2SnCl_2 is the product of the further reaction [55]. Et_3SnCl, Et_2SnCl_2, $EtSnCl_3$ and tristannane $ClEt_2SnSnEt_2SnEt_2Cl$ are formed in the reaction between Sn_2Et_6 and $SnCl_4$ [270]. The proposed reaction scheme implies no oxidative cleavage of the Sn-Sn-bond within the initial distannane:

$$\mathrm{Sn_2Et_6} + \mathrm{SnCl_4} \longrightarrow \mathrm{Et_5Sn_2Cl} + \mathrm{EtSnCl_3} \longrightarrow$$
$$\longrightarrow (\mathrm{Et_2SnCl})_2 + \mathrm{Et_2SnCl_2}$$

$$\mathrm{Et_5Sn_2Cl} \rightleftharpoons \mathrm{Et_3SnCl} + \mathrm{Et_2Sn}$$

$$(\mathrm{Et_2SnCl})_2 \rightleftharpoons \mathrm{Et_2SnCl_2} + \mathrm{Et_2Sn}$$

$$(\mathrm{Et_2SnCl})_2 + \mathrm{Et_2Sn} \longrightarrow \mathrm{ClEt_2SnSnEt_2SnEt_2Cl}$$

An independent experiment confirmed the disproportionation reaction:

$$2(\mathrm{Et_2SnCl})_2 \longrightarrow \mathrm{Et_2SnCl_2} + \mathrm{ClEt_2SnSnEt_2SnEt_2Cl}$$

Sn_2Me_6 And $SnCl_4$ react to form Me_3SnCl, Me_2SnCl_2, $MeSnCl_3$ and $SnCl_2$, and this was accounted for by assuming the competing reactions of Sn-Sn- and Sn-C-bond cleavage [162]:

$$2Me_3SnCl + SnCl_2 \longleftarrow Sn_2Me_6 + SnCl_4 \longrightarrow Me_5Sn_2Cl + MeSnCl_3$$

$$Me_5Sn_2Cl \longrightarrow Me_3SnCl + Me_2Sn$$

$$Me_2Sn + SnCl_4 \longrightarrow Me_2SnCl_2 + SnCl_2$$

Reaction of Pb_2Ph_6 and $Pb_2(2\text{-}MeC_6H_4)_6$ with $AlCl_3$ led to Ar_4Pb and $PbCl_2$; the following reaction scheme was assumed [237,307]:

$$Pb_2Ar_6 + AlCl_3 \longrightarrow Ar_4Pb_2Cl_2 \longrightarrow Ar_4Pb + PbCl_2$$

Thus, cleavage of the Pb-C-bonds alone (and not Pb-Pb) was assumed under the action of $AlCl_3$. BF_3, $MeBF_2$ and B_2H_6 were found to catalyse the Sn_2Me_6 disproportionation [315]:

$$Sn_2Me_6 \longrightarrow Me_4Sn + \frac{1}{n}(Me_2Sn)_n$$

The reaction with BF_3 also led to $MeBF_2$ and Me_3SnBF_4. Under forcing conditions the less methylated polystannanes corresponding to the empirical formulae $(Sn_5Me_2)_n$ and $(SnMe_{1,45})_n$ were obtained. The reactions of Sn_2Me_6 with BCl_3 and $PhBCl_2$ resulted in Me_4Sn, Sn^0 and RMeBCl (R=Cl,Ph) [316]. The reaction scheme suggested

$$RBCl_2 + Sn_2Me_6 \longrightarrow RClBSnMe_3 \longrightarrow RMeBSnMe_2Cl \longrightarrow$$
$$\longrightarrow Me_2Sn \longrightarrow Me_4Sn + Sn^0$$

involves an intramolecular exchanges of Cl- and Me-groups between B and Sn atoms. The possibility of dealkylation was not, however, discussed by the authors of [316].

It has been already mentioned that Si_2Et_6 and Ge_2Et_6 disproportionate when treated with $AlHal_3$ [267-269]. Razuvaev et al. [167,268,318] in 1960-63 extensively studied disproportionation of Sn_2Et_6 and Pb_2Et_6 under the effect of Lewis acids. For instance, $AlCl_3$ is an effective catalyst for disproportionation [318]:

$$2M_2Et_6 \longrightarrow 3Et_4M + M^0 \quad (M=Sn,Pb)$$

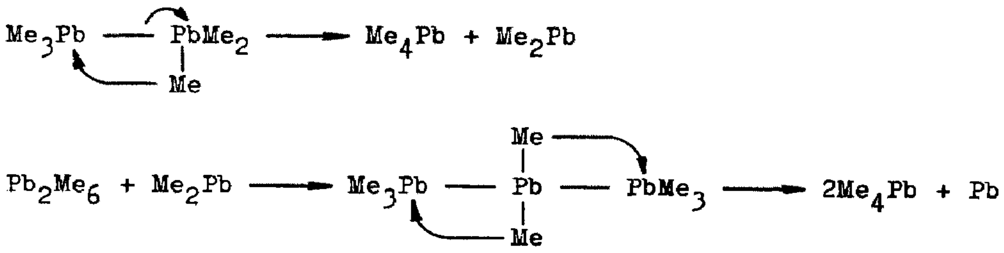
Sn_2Bu_6 Disproportionates in a similar way [227]. In the case of Sn_2Et_6 (but not of Pb_2Et_6) perethylpolystannanes $(Et_2Sn)_n$ can serve as reaction intermediates, and can be isolated [318].

From these data the conclusion can be drawn that the reactions of organic distannanes and diplumbanes with non-oxidizing Lewis acids proceed generally by disproportionation and result in M-M- and M-C-bond cleavage. It is noteworthy that similar reactions of organic disilanes and digermanes (proceeding under more forcing conditions, or with more strong electrophiles) generally produce compounds of the types R_5M_2X, or $XR_2M\text{-}MR_2X$, whereas tin and lead OBMC produce no such compounds. (With certain reservations the same conclusion holds for OBMC protolysis; see Section II). The assumption that in the reactions involving Sn_2R_6 and Pb_2R_6, the initially formed derivatives R_5M_2X or (and) $R_4M_2X_2$, disproportionate to give R_3MX (R_2MX_2) appears to be justified.

First, we should note the well known disproportionation of organic diplumbanes [16,91,127,243,319]:

$$2Pb_2R_6 \longrightarrow 3R_4Pb + Pb^o$$

The following scheme was proposed for Pb_2Me_6 disproportionation [16,243]:



$$Me_3Pb - \underset{\displaystyle Me}{\underset{|}{PbMe_2}} \longrightarrow Me_4Pb + Me_2Pb$$

$$Pb_2Me_6 + Me_2Pb \longrightarrow Me_3Pb - \overset{\displaystyle Me}{\overset{|}{\underset{\displaystyle Me}{\underset{|}{Pb}}}} - PbMe_3 \longrightarrow 2Me_4Pb + Pb$$

Thermolysis of $Me_3SnSnEt_3$ (at 190°C) resulted in Me_4Sn, Et_4Sn and metallic tin, and trace quantities of Sn_2Me_6 and Sn_2Et_6 were also detected [298]. Mixed OBMC - R_3PbMR_3 - are unstable [42,91, 167,286].

It is well known that organic derivatives of disilanes and digermanes having the general formula R_5M_2X or R_2XMMR_2X, disproproportionate on heating [79,169,223,274]:

$$(Me_2SiOMe)_2 \longrightarrow Me_2Si(OMe)_2 + MeO(SiMe_2)_nOMe \quad (n=3\div5)$$

$$Me_5Si_2CN \longrightarrow Me_3SiCN + Me_{2n+1}Si_nCN \quad (n\leqslant8)$$

$$Et_5Ge_2Cl \longrightarrow Et_3GeCl + Et_{2n+1}Ge_nCl \quad (n=3;4)$$

$$(Et_2GeCl)_2 \longrightarrow Et_2GeCl_2 + Cl(GeEt_2)_3Cl$$

The involvement of $R_2Si(R_2Ge)$ in most of the reactions either has been proved or is self-evident. The elimination of germylenes from organic germylstannanes was also reported [177,292].

$$(MeO)_3GeSnBu_3 \longrightarrow Ge(OMe)_2 + Bu_3SnOMe$$

$$GeXY + Bu_3SnCl \rightleftharpoons Bu_3SnGeXYCl \quad (X,Y=Hal,RO)$$

$$XGeCl + Me_3SnR \longrightarrow RClXGeSnMe_3 \longrightarrow Me_3SnCl + RGeX$$

$$(X=Cl,Et;\ R=CCl_3,\ CH_2CH=CH_2)$$

The susceptibility of tin-containing OBMC to disproportionation, in the first place, the decreased stability and increased reactivity of tin- and lead-containing organic compounds, in the second place, and, finally, the common phenomenon of disproportionation of substituted OBMC (e.g., of the R_5M_2X and $R_4M_2X_2$ type), enable one to suggest that it is the initial disproportionation of the compounds $R_nM_2X_{6-n}$ (n=4,5; M=Sn,Pb) that is responsible for the observed set of products.

Disproportionation of Et_5Sn_2Cl, Et_5Sn_2OH, and Bu_5Sn_2OAc proceeds readily at low temperatures [55]:

$$R_5Sn_2X \longrightarrow R_3SnX + \frac{1}{n}(R_2Sn)_n.$$

$(Et_2SnCl)_2$ Disproportionates (at 20°C) to form Et_2SnCl_2 and $Cl(Et_2Sn)_3Cl$ [270]. Ph_4Pb And $Pb(OAc)_2$ were obtained on heating $(Ph_2SnOAc)_2$ [77]. Important results concerning the disproportionation of R_5Sn_2Hal and $R_4Sn_2Hal_2$ were achieved during the last decade, mainly by Neumann et al. Thus the compounds $(Bu_2SnX)_2$ (X=H,Cl,Br,OAc) disproportionate on heating, giving Bu_2SnX_2 and $(Bu_2Sn)_n$ [264]. $(Me_2SnCl)_2$ Disproportionates according to the same scheme even at room temperature [278]; $Me_3SnSnEt_2Br$ is also unstable and undergoes disproportionation [154]. Et_5Sn_2Br Disproportionates at 100°C, and Me_5Sn_2Br at -30°C. Carrying out the disproportionation reaction in a medium of Et_4Sn, Sn_2Me_6 or Sn_2Et_6 results in the incorporation of the R_2Sn species into the Sn-Sn and Sn-C-bonds of the organotin compounds to give peralkylpolystannanes [278]. The equilibrium:

$$(Me_2SnBr)_2 \rightleftharpoons Me_2SnBr_2 + \frac{1}{n}(Me_2Sn)_n$$

was found to be slow at 310 K in PhH or $CHCl_3$ solution [87] (see also [174,259]). The results are important for understanding the Sn_2Me_6 disproportionation reactions under the action of Me_3SnX,

Me_2SnCl_2 and some other similar Lewis acids.

Sn_2Me_6 Disproportionates when treated with Me_3SnCl in MeOH solution to form Me_4Sn and a residue of $(Me_2Sn)_n$ [51,226]. According to the kinetic equation:

$$W = k[Sn_2Me_6][Me_3SnCl]^{0,5}$$

the catalytic reagent was concluded to be the dissociated form: $Me_3SnCl \rightleftharpoons Me_3Sn^+ + Cl^-$. The reactions:

$$Sn_2Me_6 + Et_3SnCl \longrightarrow Et_3SnMe + Me_3SnCl + \frac{1}{n}(Me_2Sn)_n$$

$$Sn_2Me_6 + Me_2SnCl_2 \longrightarrow 2Me_3SnCl + \frac{1}{n}(Me_2Sn)_n$$

were also carried out. Under these conditions Sn_2Et_6 does not react with Et_3SnCl [51].

Wells et al. [13-17] investigated the disproportionation of Sn_2Me_6 under the action of R_3SnHal, as well as a number of related transformations. Thus the nature of the catalysed disproportionation of Sn_2Me_6 under the action of Me_3SnHal was established [13]:

$$Sn_2Me_6 \xrightarrow[Me_3SnX]{} Me_4Sn + \frac{1}{n}(Me_2Sn)_n \quad (X=Cl,Br,I)$$

The second order kinetics of the reaction (MeOH; 30°C; NMR spectroscopy) indicate catalysis by the undissociated Me_3SnX.

The following reaction was also carried out:

$$Sn_2(CH_3)_6 + (CH_2{=}CH)_3SnCl \longrightarrow (CH_2{=}CH)_3SnCH_3 + (CH_3)_3SnCl + \frac{1}{n}[(CH_3)_2Sn]_n$$

The Sn-Sn-bonds are unaffected under the action of $(CH_2{=}CH)_3SnCl$. A reinvestigation of the disproportionation of Sn_2Me_6 under the action of Me_3SnCl gives the following kinetics [14]:

$$W = k_2[Sn_2Me_6][Me_3SnCl] + k_{1,5}[Sn_2Me_6][Me_3SnCl]^{0,5}$$

This corresponds to catalysis by both undissociated Me_3SnCl and the Me_3Sn^+ ion. $Sn_2(CH_3)_6$ and $(CD_3)_4Sn$ were found to react with $(CH_3)_3SnCl$ at similar rates which implies that the first stage of the reaction - the alkyl exchange -

$$Sn_2Me_6 + Me_3SnCl \rightleftharpoons Me_4Sn + Me_5Sn_2Cl$$

is slow and rate-determining. Further, Me_5Sn_2Cl eliminates Me_2Sn, which inserts into the Sn-Sn- and Sn-Cl-bonds of the organotin compounds to give, ultimately, permethylpolystannanes. Permethylpolystannanes formed by disproportionation of Sn_2Me_6 under the effect of $(CD_3)_3SnCl$ (in MeOH solution) contain no CD_3-groups. It follows that the Sn-Sn-bond in $Sn_2(CH_3)_6$ is unaffected by $(CD_3)_3SnCl$ since $(CH_3)_3SnSn(CD_3)_3$ formed in the latter case would disproportionate to give labelled $(Me_2Sn)_n$. It likewise follows that $(CH_3)_2Sn$ is not inserted into the Sn-C-bond of $(CD_3)_3SnCH_3$ formed at the first stage, since the $Sn_2(CH_3)_3(CD_3)_3$ produced would disproportionate to give labelled $(Me_2Sn)_n$ [14].

A parallel study of the disproportionation of Sn_2Me_6 was performed in [162]. The branched character of the permethylpolystannanes obtained was shown by the bromination method (see below). The sequence of the catalytic activity found for Me_3SnX was as follows: $BF_4 > NO_3 > Cl \sim Br$. The sequence of the solvent effect on the reaction rate ($PhNO_2 > PhCN \sim MeOH > PhH > 1,4$ - dioxane) follows the order of the competing effect of the polar and solvating properties of solvents on the alkyl exchange rate at the tin atom. In polar solvents - PhCN and $PhNO_2$ - using NMR spectroscopy it has been possible to detect the $Me_5Sn_2BF_4$ intermediate resulting from the fast methyl exchange:

$$Sn_2Me_6 + Me_3SnBF_4 \rightleftharpoons Me_4Sn + Me_5Sn_2BF_4$$

The proposed scheme for the disproportionation reaction is similar, on the whole, to that of the authors of [14], and involves elimination of Me_2Sn from Me_5Sn_2X followed by the stannylene incorporation reactions.

The following evidence was obtained by studying the reactions between Sn_2Me_6 and Me_2SnCl_2 [17]. The products obtained are Me_3SnCl and $(Me_2Sn)_n$, as well as the intermediate $(Me_2SnCl)_2$ which further undergoes disproportionation to give $(Me_2Sn)_n$. Reaction between $Sn_2(CH_3)_6$ and $(CD_3)_2SnCl_2$ leads to $(CH_3)_2SnCl_2$ and the CD_3-containing permethylpolystannanes (mass spectrometry data). This fact was explained by elimination of Me_2Sn from the unstable Me_5Sn_2Cl formed, the former being able to incorporate reversibly into the reagents' bonds:

$$(CH_3)_2Sn + (CD_3)_2SnCl_2 \rightleftharpoons Cl(CH_3)_2SnSn(CD_3)_2Cl \rightleftharpoons$$
$$\rightleftharpoons (CH_3)_2SnCl_2 + (CD_3)_2Sn$$

Indeed, the (^1H, ^{13}C, ^{119}Sn)-NMR spectra reveal the broadening of the Me_2SnCl_2 and $(Me_2SnCl)_2$ resonance signals (unlike Sn_2Me_6 or Me_3SnCl), with $(Me_2SnCl)_2$ being shown to be a secondary source of Me_2Sn. It appears that Me_5Sn_2Cl serves as the principal source of Me_2Sn.

$$Sn_2Me_6 + Me_2SnCl_2 \longrightarrow Me_3SnCl + Me_5Sn_2Cl$$
$$Me_5Sn_2Cl \longrightarrow Me_3SnCl + Me_2Sn$$
$$Sn_2Me_6 + Me_2SnCl_2 \rightleftharpoons (Me_2SnCl)_2$$
$$Sn_2Me_6 + (Me_2SnCl)_2 \longrightarrow 2Me_5Sn_2Cl$$
$$Me_2SnCl_2 + (n-1)Me_2Sn \longrightarrow Cl(Me_2Sn)_nCl$$
$$Cl(Me_2Sn)_nCl + Sn_2Me_6 \quad (\text{or } Me_4Sn) \longrightarrow Sn_nMe_{2n+2}$$

A valuable comparative analysis of the reactivity of Sn_2Me_6, Me_3SnCMe_3 and Me_4Sn, on the one hand, and Me_3SnCl, Me_2SnCl_2 and $(Me_2SnCl)_2$ on the other, was performed.

Reactions between Sn_2Me_6 and methyltin chlorides:

$$Sn_2Me_6 + Me_2SnCl_2 \longrightarrow 2Me_3SnCl + \frac{1}{n}(Me_2Sn)_n$$

$$Sn_2Me_6 + MeSnCl_3 \longrightarrow Me_3SnCl + Me_2SnCl_2 + \frac{1}{n}(Me_2Sn)_n$$

also involve dealkylation followed by the subsequent disproportionation of Me_5Sn_2Cl formed. Reactions between $Me_3SiSnMe_3$ and Me_nSnCl_{4-n} ($n=1-3$) give $Me_3SiSnMe_2Cl$:

$$Me_3SiSnMe_3 + Me_3SnCl \rightleftharpoons Me_3SiSnMe_2Cl + Me_4Sn$$
$$Me_3SiSnMe_3 + Me_2SnCl_2 \longrightarrow Me_3SiSnMe_2Cl + Me_3SnCl$$
$$Me_3SiSnMe_3 + MeSnCl_3 \longrightarrow Me_3SiSnMe_2Cl + Me_2SnCl_2$$

The reactivity sequence is $MeSnCl_3 > Me_2SnCl_2 > Me_3SnCl$. The rates of the reactions of $Me_3SiSnMe_3$, Sn_2Me_6 and Me_4Sn with each of three methyltin chlorides (in PhH, $PhNO_2$, or MeOH solution) are close to each other, which permits the conclusion that Me_3Si, Me_3Sn - substituents offer no steric hindrance (as compared with the Me group) to electrophilic dealkylation in $RSnMe_3$ (R=Me,Me_3Si,

Me_3Sn) [162].

More recently reactions of Me_3MSnMe_3 (M=Si,Ge) with Me_3SnCl and Me_2SnCl_2 (in MeOH solution) were also investigated [186]:

$$Me_3SiSnMe_3 + Me_3SnCl \longrightarrow Me_4Sn + Me_3SiSnMe_2Cl$$
$$Me_3SiSnMe_2Cl \longrightarrow (Me_2Sn)_n + Me_3SiCl$$
$$Me_3SiSnMe_3 + Me_2SnCl_2 \longrightarrow Me_3SnCl + Me_3SiX + (Me_2Sn)_n + Me_4Sn$$
$$Me_3GeSnMe_3 + Me_3SnCl \longrightarrow Me_3GeCl + (Me_2SnCl)_2 + Me_4Sn$$
$$Me_3GeSnMe_3 + Me_2SnCl_2 \longrightarrow Me_3SnCl + Me_3GeCl + $$
$$+ (Me_2SnCl)_2 + Me_3GeSnMe_2Cl$$

Sn_2Me_6 And Me_3PbCl react giving Me_4Sn, Me_4Pb and $PbCl_2$. The reaction mechanism is as follows [15]:

$$Sn_2Me_6 + Me_3PbCl \longrightarrow Me_4Pb + Me_5Sn_2Cl$$
$$Me_5Sn_2Cl \longrightarrow Me_3SnCl + Me_2Sn$$
$$Me_3SnCl + Me_4Pb \longrightarrow Me_4Sn + Me_3PbCl$$
$$Me_3PbCl + Me_2Sn \longrightarrow Me_3PbSnMe_2Cl \longrightarrow ClMe_2PbSnMe_3 \longrightarrow$$
$$\longrightarrow Me_3SnCl + Me_2Pb$$
$$Me_2Pb + 2Me_3PbCl \longrightarrow 2Me_4Pb + PbCl_2$$

Reactions of Pb_2Me_6 with Me_3SnCl and Me_3PbCl are similar stoichiometrically:

$$Pb_2Me_6 + 2Me_3PbCl \longrightarrow 3Me_4Pb + PbCl_2$$
$$Pb_2Me_6 + 2Me_3SnCl \longrightarrow Me_4Pb + 2Me_4Sn + PbCl_2$$

For the first reaction the kinetic equation obtained was:

$$W = (13{,}7 \pm 1{,}6)[Pb_2Me_6][Me_3PbCl] + (0{,}21 \pm 0{,}03)[Pb_2Me_6][Me_3PbCl]^{0.5}$$

thus Me_3PbCl and Me_3Pb^+ act as electrophiles. The corresponding rate constants for Me_3PbNO_3 are equal to (at 25°C) (24.05±0.04) l/mol.s, and (1.93±0.01) $l^{0.5}/mol.s^{0.5}$, respectively. Comparing the rate constants (k_2 and $k_{1.5}$) for Me_3PbCl and Me_3PbNO_3, one can see that the latter reacts more readily because of the greater reactivity of undissociated Me_3PbNO_3 as compared with undissociated Me_3PbCl, and because of the greater degree of ionization of the nitrate as compared with the chloride. Other

Me_3PbX(X=OH,OMe,CN) compounds react (at lower rate) according to the same stoichiometric equation. The general reaction scheme was proposed [15]:

$$Pb_2Me_6 + Me_3MCl \longrightarrow Me_4M + Me_5Pb_2Cl$$
$$Me_5Pb_2Cl \longrightarrow Me_3PbCl + Me_2Pb$$
$$Me_2Pb + 2Me_3MCl \longrightarrow 2Me_4M + PbCl_2$$
$$(Me_3SnCl + Me_4Pb \rightleftharpoons Me_4Sn + Me_3PbCl)$$

Sn_2Me_6 Reacts with $Co_2(CO)_8$, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ according to the equation [233]:

$$Sn_2Me_6 + M_2(CO)_{2n} \longrightarrow 2Me_3SnM(CO)_n$$

Analogously, $Et_3SnCo(CO)_4$ and $ClEt_2SnCo(CO)_4$ are obtained from Sn_2Et_6 and $(Et_2SnCl)_2$ respectively. In THF, with more pronounced solvating properties, the following reaction takes place [129]:

$$Sn_2Me_6 + Co_2(CO)_8 \longrightarrow 1{,}0Me_3SnCo(CO)_4 + 0{,}5Me_4Sn + \\ + 0{,}3Me_2Sn[Co(CO)_4]_2$$

It was observed that the first product does not disproportionate to yield the last two. In the presence of catalytic amounts (10%) of $Co_2(CO)_8$, Sn_2Me_6 disproportionates to give Me_4Sn and "$(Me_2Sn)_n$" (the latter being branched permethylpolystannanes, as proved by the formation of Me_3SnBr, Me_2SnBr_2 and $MeSnBr_3$ by bromolysis). The following scheme was proposed for the disproportionation reaction:

$$Co_2(CO)_8 + THF \longrightarrow Co(CO)_4^+\ THF + Co(CO)_4^-$$
$$Co(CO)_4^+\ THF + Sn_2Me_6 + Co(CO)_4^- \longrightarrow Me_5Sn_2Co(CO)_4 + \\ + MeCo(CO)_4 + THF$$
$$Me_5Sn_2Co(CO)_4 \longrightarrow Me_3SnCo(CO)_4 + Me_2Sn \quad (\longrightarrow \text{polymer})$$
$$Me_3SnCo(CO)_4 + MeCo(CO)_4 + THF \longrightarrow Me_4Sn + Co(CO)_4^+\ THF + \\ + Co(CO)_4^-$$

The catalysts for the Sn_2Me_6 disproportionation are $Mn_2(CO)_{10}$ and $ICo(CO)_4$ but not $CoBr_2$. Sn_2Ph_6, Sn_2Et_6 And Ge_2Et_6 undergo no disproportionation when treated with $Co_2(CO)_8$ [129].

IV. TETRACYANOETHYLENE AND OTHER π-ACCEPTORS

In 1973 two groups of investigators [122,123] simultaneously discovered a donor-acceptor interaction of organobi- and polymetallic compounds of the IVB group with $C_2(CN)_4$ (TCNE) by observation of the charge transition bands (CTB) in the electronic absorption spectra. Within the donor-acceptor complexes formed the organo-element compounds are the σ-donors. The CTB energies correlate linearly with the IP of the electron-donors [122,123,125,130,209]. Upon irradiation, the TCNE anion-radical is formed, and its ESR signal is lost on termination of the irradiation [123]. Cyclic disilanes $Me_2\overline{Si(CH_2)_nSi}Me_2 (n=3-5)$ also form DAC with TCNE; E_{CT} correlates linearly with the activation enthalpies of the reaction of the cyclodisilanes used (as well as Si_2Me_6) and $3\text{-}ClC_6H_4CO_3H$ [124]:

$$\Delta H^{\neq} = 0.737\ E_{CT} - 36.8\ \text{kcal/mol}\ (r = 0.991)$$

The DAC of aryl-containing organodisilanes with TCNE were also studied; it was shown that the regularities established on variation of IP and E_{CT} for organodi- and poly-silanes are well explained by the $\sigma\sigma$- and $\sigma\pi$-interactions within the OEC molecule [128,179]. Ge_2Ph_6 But not $(C_6F_5)_3GeGeEt_3$ and $(C_6F_5)_2GeHGeH(C_6F_5)_2$ yield CTB with TCNE [135].

Such compounds as Bu_4Ge, Alk_4Sn, Sn_2Alk_6, Et_4Pb and Me_2Hg turned out to form DAC with TCNE, too, as well as with quinones [122,125,130]. Sn_2Ph_6 [147] And Sn_2Me_6 [125,126] can reduce TCNE to the anion-radical; in the latter case the reaction is completed with the precipitation of a black sediment [123,130]. Sn_2Me_6 And Sn_2Bu_6 react with TCNE and TCNQ to give the ion pair $R_3Sn^+A^{-\bullet}$ [139]. Sn_2Ph_6 Does not react with TCNE, while with TCNQ it can form the complex $[Sn_2Ph_6 \cdot TCNQ]$ [139]. Under the action of TCNE and TCNQ, Pb_2Me_6 undergoes oxidative disproportionation to give the Pb^{2+} salts, Me_2Pb and CH_4 [143].

The reaction of Sn_2Me_6 and TCNE was studied in more detail [141]. The reaction product is the complex $Me_3SnC(CN)_2C(CN)_2SnMe_3 \cdot THF$ (isolated from the CH_2Cl_2 solution in 70% yield), which, when kept or dissolved in THF, undergoes spontaneous conversion into $Me_3SnN{=}C{=}C(CN)C(CN)_2^{\bullet}$. Thus, it is homolysis of the unstable adduct that is responsible for the radical production in the reaction considered, and not a one-electron oxidation of the OBMC.

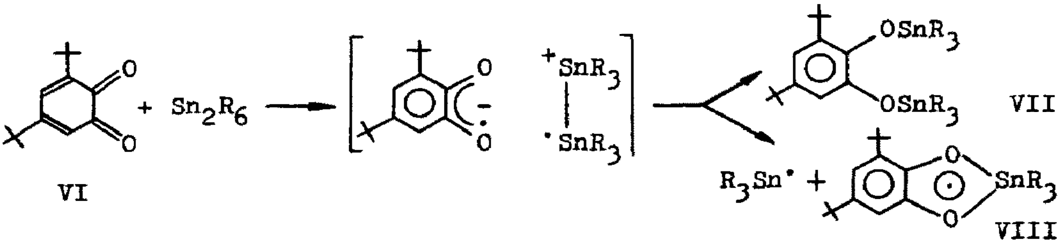
Reactions between Sn_2R_6 (R=Me,Bu,Ph) and chloranil, and other quinones give $1,4\text{-}C_6X_4(OSnR_3)_2$ [139,146]* The ESR spectral data enabled the authors to identify the intermediate radicals as semiquinones and aroxyls; the following reaction mechanism was proposed [146]:

$$Sn_2R_6 + C_6X_4O_2 \rightleftharpoons DAC \longrightarrow [Sn_2R_6^{+\cdot}\ {}^{-\cdot}C_6X_4O_2] \longrightarrow$$

$$\longrightarrow [R_3SnOC_6X_4O^{\cdot}\ {}^{\cdot}SnR_3] \longrightarrow 1,4\text{-}C_6X_4(OSnR_3)_2$$

The reaction rates for quinones correlate with their electron affinities.

The interaction of 3,5- and 3,6-di-tert-butyl-1,2-benzoquinones with Sn_2R_6 (R=Me,Et,Bu,Ph) was also studied [144]. 4 Moles of quinone per 1 mole of Sn_2R_6 are involved in the reaction. The first stage of the process is the electron transfer, proved by the current generation of an electrochemical cell involving benzoquinone VI and Sn_2Et_6. The ion-radical pair formed can yield the radical products:



$$VI + VII \longrightarrow 2VIII; \quad R_3Sn^{\cdot} + VI \longrightarrow VIII$$

The radical VIII, involving a 5-coordinated tin atom, can react further, to give catechol derivatives.

9,10-Phenanthraquinone (IX) reacts at low temperature with Sn_2Me_6 and Pb_2Me_6 to give the radical X. The similar product, but only on heating, is provided by Pb_2Ph_6. On the other hand, Pb_2Ph_6 and TCNE were found to form the DAC, λ_{max}^{CTB} = 300 nm. When irradiating the mixture of Pb_2Ph_6, TCNE and IX at 650 nm, where the DAC $[Pb_2Ph_2 \cdot TCNE]$ is the only absorbing species, the ESR spectrum reveals the radical X ($R_3M=Ph_3Pb$). In the absence of TCNE the irradiation does not lead to this product, while Pb_2Ph_6

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* Sn_2Me_6 And chloranil also led to $1,4\text{-}C_6Cl_4(OSnMe_3)_2$ (and not to $4\text{-}Me_3SnOC_6Cl_4O^{\cdot}$, as was previously suggested [139]) [146].

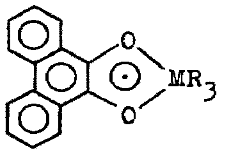
and quinone do not react at all. It thus seems to be established that it is the irradiation of the DAC within the charge-transfer band that results in the Pb_2Ph_6 homolysis. The following reaction scheme was proposed [145]:

$$Pb_2Ph_6 + C_2(CN)_4 \xrightarrow{h\nu} [Pb_2Ph_6^{\bullet +} \ {}^{-\bullet}C_2(CN)_4]$$

$$\longrightarrow [Ph_3Pb^{\bullet} \quad Ph_3PbC_2(CN)_4^{\bullet}]$$

$$\longrightarrow Ph_3Pb^{\bullet} + Ph_3PbC_2(CN)_4^{\bullet}$$

$$Ph_3Pb^{\bullet} + IX \longrightarrow X$$



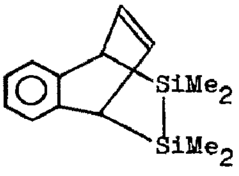
X

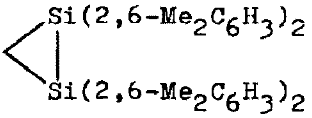
V. PEROXIDE COMPOUNDS

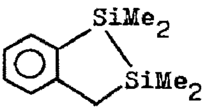
Organodisilanes react smoothly with $PhCO_3H$ to give the corresponding disiloxanes with good yields. A linear correlation between lg k_2 and the σ^+-constants of Ar substituents was established for the oxidation of six $ArSi_2Me_5$ compounds ($\rho = -0.29$) [320]. The activation parameters for the reactions studied were determined [64]. The kinetics of the reactions between $PhCO_3H$ and a wide series of disilanes was also investigated [156].

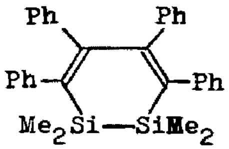
Reaction between $Me_5Si_2CH{=}CH_2$ and $3\text{-}ClC_6H_4CO_3H$ results in $Me_5Si_2\overline{CHCH_2O}$ (the main product), $Me_3SiOSiMe_2\overline{CHCH_2O}$ and $Me_3SiOSiMe_2CH{=}CH_2$. The first stage of the reaction is epoxidation of the C=C-bond, and the oxirane moiety formed facilitates further oxidation of the Si-Si-bond. $Me_5Si_2CH_2CH{=}CH_2$ When treated with $3\text{-}ClC_6H_4CO_3H$ gives rise to $Me_3SiOSiMe_2CH_2CH{=}CH_2$ and $Me_5Si_2CH_2CH_2CHO$ (the product of acid-catalyzed rearrangement of $Me_5Si_2CH_2\overline{CHCH_2O}$). $Me_5Si_2CH_2CH_2SEt$ is oxidized to $Me_5Si_2CH_2CH_2SO_2Et$ [152].

A number of cyclic organodisilanes shown below are oxidized by $3\text{-}ClC_6H_4CO_3H$ to the corresponding disiloxanes [28,202,244, 310].



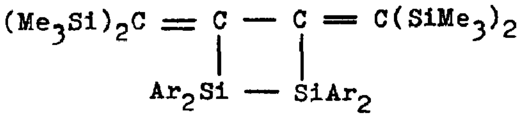


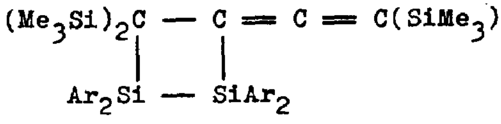




The disilacyclobutanes shown below are oxidized by $3\text{-}ClC_6H_4CO_3H$

to the corresponding disiloxanes when Ar=Ph [69,183], para- and meta-tolyl, and not when Ar is the sterically overcrowded ortho-tolyl [88].





Cyclic disilanes I, III react smoothly with $PhCO_3H$ and $(Me_3SiO)_2$ (with III being more active that I) to give the corresponding disiloxanes with unchanged configurations. Both cis- and trans-isomers of 9,10-dimethyl-9,10-disiladecalin are oxidized by the same reagents to form cis-disiloxanes, the yield from the trans-disilane (involving total stereomutation) being lower than from the cis-isomer [238,239]. The oxidation of a series of disilanes, $Me_nF_{3-n}SiSiMe_mF_{3-m}$ (n,m = 1 to 3) and $Me_2\overline{Si(CH_2)_kSi}Me_2$ (k = 3 to 5), with $(Me_3SiO)_2$ give the corresponding disiloxanes [59]. The reaction:

$$Ge_2R_6 + Bu^tOOH \longrightarrow R_3GeOH + R_3GeOBu^t \longrightarrow (R_3Ge)_2O + $$
$$+ Bu^tOH \ (R=C_6F_5)$$

has been reported [201]. Reactions between OBMC and ozone are reviewed in [240].

The reaction between Sn_2R_6 and peroxides has been thoroughly studied. Sn_2Et_6 Reacts with $(PhCO_2)_2$ (in PhH) to give $PhCO_2SnEt_3$ (as the main product), and $(PhCO_2SnEt_2)_2O$. The reaction seems to proceed according to a latent-radical mechanism since the system Sn_2Et_6 + $(PhCO_2)_2$ initiates the polymerization of CH_2=CHCN [167, 303,309]. The thermochemistry of the reaction

$$Sn_2Et_6 + (PhCO_2)_2 \longrightarrow 2PhCO_2SnEt_3; \quad \Delta H = -(108\pm5)\text{kcal/mol}$$

has been studied [83]. Reactions of Sn_2Et_6 with acyl peroxides proceed according to the equation [167,234,235,303]:

$$Sn_2Et_6 + RCO_2OR' \longrightarrow RCO_2SnEt_3 + R'OSnEt_3$$

apparently without radical formation. The reaction between Sn_2Et_6 and $(Et_3SnO)_2$ proceeds along both molecular and radical reaction pathways [263]:

$$Sn_2Et_6 + (Et_3SnO)_2 \begin{array}{l} \nearrow 2(Et_3Sn)_2O \\ \searrow Et_3Sn^{\bullet} + (Et_3Sn)_2O + Et_3SnO^{\bullet} \end{array}$$

Radical processes likewise contribute in the reaction [313]:

$$Sn_2Et_6 + Et_3SnOOBu^t \longrightarrow (Et_3Sn)_2O + Et_3SnOBu^t$$

Neumann et al. [314] reported a detailed study of the reaction of Sn_2Me_6 with Ac_2O_2 and $(PhCO_2)_2$. The main product of the first reaction (at 20°C) was Me_3SnOAc (95%); small quantities of CO_2 and Me_4Sn were also produced. In the presence of the radical inhibitor, Bu^tBr, Me_3SnOAc alone was formed (100%). $(PhCO_2)_2$ reacts with Sn_2Me_6 more slowly than Ac_2O_2 to give $PhCO_2SnMe_3$ as the main product. The by-products - Me_4Sn, Me_3SnPh and CO_2 - result from the radical process, as proved through its inhibition with Bu^tBr, as well as by the ^{13}C CIDNP technique. Sn_2Et_6 And Sn_2Bu_6 react with $(PhCO_2)_2$ in a similar way to Sn_2Me_6. Pb_2Et_6 Reacts at high rates with the peroxide compounds according to the scheme [168]:

$$Pb_2Et_6 + ROOR' \longrightarrow Et_3PbOR + Et_3PbOR'$$

Bu_3PbOAc Was isolated in the reaction with HO_2Ac [193]. From Pb_2R_6 (R=Bu,Ph,4-MeC_6H_4) and $R'CO_3H$ (R'=Me,n-C_7H_{15},n-$C_{11}H_{23}$, $BuEtCHCH_2$,Ph) the six derivatives, $R'CO_2PbR_3$, were obtained; Pb_2Ph_6 and perphthalic acid reacted to give 2-$Ph_3PbO_2CC_6H_4CO_2H$ [312].

VI. ELECTROPHILIC (AND OXIDIZING) REAGENTS OF OTHER TYPES

The compounds M_2Et_6 undergo dealkylation when reacted with (AlkHal + $AlHal_3$); the product composition is controlled by the stability of Et_5M_2Hal (see Section III). Thus the reaction between Si_2Et_6 and i-PrBr in the presence of catalytic quantities of $AlBr_3$ gave Et_5Si_2Br (72%) [267]; Ge_2Et_6 under the same conditions gave Et_5Ge_2Br (50%), Et_4Ge and Et_3GeBr [269]. Sn_2Et_6, i-PrCl and $AlCl_3$ react to give Et_3SnCl and Et_4Sn [318], and PrCl and PrBr react in the same way [268].

The organodisilanes Si_2Me_6, Si_2Et_6, $(Et_2SiMe)_2$ and $Me_3SiSiPh_3$ react with RCOCl and $(RCO)_2O$ in the presence of $AlCl_3$ to give ketones in fair yields [94]. Thus the reaction of $Me_3SiSiPh_3$

with EtCOCl leads to PhCOEt (90%). The silicon-containing compounds were not isolated. Later, it was shown that, varying the reaction conditions, Me_5Si_2Cl (85%) 1,2-$Me_4Si_2Cl_2$ (87%), or 1,1,2-$Me_3Si_2Cl_3$ (74%) could be obtained from Si_2Me_6 and AcCl (with $AlCl_3$ as a catalyst) [157,196]. In the absence of Lewis acids Sn_2Me_6 reacts with CF_3COCl or $(CF_3CO)_2O$ to give Me_4Sn, $CF_3CO_2SnMe_3$ and CO; the reaction with CF_3COI led to Me_3SnCF_3 (74%), Me_4Sn, Me_3SnI and CO [30]. Sn_2Et_6 Reacts with PhCOCl to form Et_3SnCl (as a main product), Et_2SnCl_2 and $PhCO_2C(Ph)=$ $=C(Ph)O_2CPh$ [318].

$MeSO_3SiMe_5$ (50%) And Me_3SiCl were obtained by the reaction between Si_2Me_6 and $ClSO_3SiMe_3$; $(MeSO_3SiMe_2)_2$ was also synthesized [260]. Sn_2Et_6 Reacts with $PhSO_2Cl$ to give Et_3SnCl and Et_3SnSO_2Ph [167,318]. Reactions of Pb_2Et_6 with SO_2Cl_2, $SOCl_2$, SCl_2 or S_2Cl_2 resulted in Et_3PbCl [291]. The compounds Sn_2R_6 react with Ph_2S_2 to form R_3SnSPh; Me_2S_2 reacts more slowly [55]. Pb_2Ph_6 And Ph_2S_2 react to give Ph_3PbSPh (and small quantities of Ph_4Pb), the reaction being catalyzed by water. In a similar way, 4-$ClC_6H_4SPbPh_3$ was synthesized [91]. Reaction of Si_2Me_6 with 5-F-uracyl (150-160°C) produced 2,4-$(Me_3Si)_2$-5-F-uracyl, which was employed in the synthesis of heterocyclic compounds [148]. Nitration of 1,4-$C_6H_4(Si_2Me_5)_2$ gave a mixture of unidentified products, which contained no 4-$Me_5Si_2C_6H_4NO_2$, while the similar reaction of $PhSi_2Me_5$ produced a complex mixture of products involving $PhNO_2$ [150]. Reactions of a series of disilanes of general formula $R_2C=CHCH(X)Si_2Me_5$ (with X = R'S, PhSe) with $Me_3O^+BF_4^-$ proceed under mild conditions to give, as a result of the Me_3Si-shift, $R_2C=CHCH(SiMe_3)SiMe_2F$; the geometric configuration in this case is retained. A high degree of stereoselectivity was observed in the case of chiral E-Me(i-Pr)C=CHCH(Si_2Me_5)SR', though the stereochemical result remains to be seen [33].

N-Bromosuccinimide cleaves the Si-Si-bonds in Si_2Me_6 [311] and $(Et_2SiMe)_2$ [262] (probably, by a molecular mechanism) to give R_3SiBr and $R_3SiN(CH_2CO)_2$; $PhSi_2Me_5$ and $(PhSiMe_2)_2$ react with NBS to form R_3SiBr, PhBr (small quantities), and $(CH_2CO)_2NH$ [311]. The reaction between N-chlorosuccinimide and Sn_2Me_6 (as well as Sn_2Bu_6) was unambiguously proved to proceed through a radical-chain mechanism [26]. Me_3SbS Reacts with Sn_2Ph_6 and $Sn_2(CH_2Ph)_6$ to give $(R_3Sn)_2S$. Ph_3SbS Reacts in a similar manner with Sn_2Ph_6 (but not with $Sn_2(CH_2Ph)_6$); Ge_2Ph_6 and Si_2Ph_6 are unaffected by R_3SbS [133]. Pb_2Ph_6 Reacts with HOCl to give Ph_3PbCl [91,140]; Ph_3PbBr and $(4\text{-}MeC_6H_4)_3PbI$ were obtained through similar reactions [140]. M_2Ph_6 (M=Pb,Sn,Ge) React with $Se(SeCN)_2$ to form either $Ph_3PbSeCN$ or $Ph_3SnNCSe$; in the case of Ge_2Ph_6 no Ge-containing compounds were isolated. In all cases Se and (small quantities of) PhSeCN were formed [266]. $Sn_2(4\text{-}MeC_6H_4)_6$, Pb_2Ph_6 And $Pb_2(4\text{-}MeC_6H_4)_6$ react with $(SCN)_2$ to give Ar_3MNCS [176]. $KMnO_4$ Oxidizes Sn_2R_6 and Pb_2Ph_6 to give $(R_3M)_2O$ [49,55,91,248,289]; titration with $KMnO_4$ in acetone allows one to determine quantitatively Pb_2Et_6 in Et_4Pb [229].

The oxidation of distannanes, Sn_2Me_6, Sn_2Bu_6, Sn_2Ph_6, and $Me_3SnSnPh_3$, by the Fe(III) complexes, $L_3Fe^{+3}3ClO_4^-$ (where L usually phenanthrolines) was studied. The reaction proceeds according to the equation:

$$Sn_2R_6 + 2Fe^{+3} \longrightarrow 2R_3Sn^+ + 2Fe^{+2}$$

The probable intermediates are cation-radicals $Sn_2R^{\cdot+}_6$. The lg k_2 values correlate with the standard oxidation potentials $E^o_{Sn_2R_6}$ All the systems studied obey the correlation:

$$\lg k_2 = -1{,}29\Sigma\sigma^* + C_L;$$

where σ^* is the value of Taft's constant for the substituent R; C_L is the reaction ratio for L_nFe^{+3}. The correlation between E_{act} and free energies for the total charge transfer was established; the slope of 0.44 corresponds to the outersphere oxidation mechanism [181].

CONCLUSIONS

The most general regularities of OBMC reactions with electrophilic reagents are summarized below. Such oxidants as halogens, peroxides, metal salts (Ag^+, Hg^{+2}, Pb^{+4} etc.) lead to oxidative cleavage of the M-M-bond in OBMC producing R_3MX. Non-oxidizing electrophiles such as Brönsted and Lewis acids usually give R_5M_2X and/or $R_4M_2X_2$ as a result of OBMC dealkylation. These compounds are quite stable in the case of silicon and germanium derivatives, and are unstable in the case of organic distannanes and diplumbanes. The distannanes undergo disproportionation to give R_3SnX (R_2SnX_2) and peralkylpolystannanes, and R_4Pb and PbX_2(or Pb^0) are formed from diplumbanes. The reactivity follows the same order (Pb > Sn > Ge > Si) for both oxidation and dealkylation of OBMC.

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