Brief Communications

Redox reactions of Ge^{II} and Sn^{II} dihalides with triethylsilane and triethylgermane

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Dihalogermylenes, dihalostannylenes, and their complexes (EI_2, $ECl_2 \cdot$dioxane, and $(CO)_5W{=}ECl_2 \cdot THF$, where E = Ge or Sn), unlike organylgermylenes, are not inserted at the Si—H (Ge—H) bond of triethylsilane (triethylgermane). The reactions of SnI_2, $ECl_2 \cdot$dioxane, and $(CO)_5W{=}ECl_2 \cdot THF$ (E = Ge or Sn) with $Et_3E'H$ (E´ = Si or Ge) occur as redox processes. Depending on the nature of the reagents, the reactions afford products of oxidative coupling ($Et_3SiSiEt_3$) and/or haloiodination (Et_3SiX and Et_3GeX) of triethylsilane (triethylgermane). The proposed mechanism of these reactions involves the electron transfer to form radical-ion pairs.

Key words: dihalogermylenes, dihalostannylenes, complexes of dihalogermylenes and dihalostannylenes with dioxane and tungsten pentacarbonyl, trialkylsilanes, trialkylgermanes, hexaalkyldisilanes, redox reactions.

The insertion of carbene analogs (silylenes, germylenes, and stannylenes) at the E—X σ-bond (E = Si, Ge, or Sn; X = Hal, C, or M) is a convenient procedure for the preparation of compounds containing the E—E´ bond (E, E´ = Si, Ge, or Sn). The insertion of germylenes at the C—Hal, E—Hal (E = Ge or Sn), H—O, H—Cl, S—S, C—E, Ge—X (X = N, O, S, or P), and C—M (M = Li, Mg, Ge, or Sn) bonds has been studied in sufficient detail.[1—3] By contrast, the insertion of germylenes at the E—H bond has not been adequately investigated. In particular, only several examples of the insertion of short-lived organylgermylenes at the B—H, Si—H, and Ge—H bonds were described.[4—12] The possibility of such reactions being performed with more readily accessible dihalogermylenes and dihalostannylenes has not been examined previously. Unlike diorganylgermylenes and diorganylstannylenes, dihalogermylenes (dihalostannylenes) can act as rather strong oxidizers in chemical reactions[13] although examples of these reactions are few in number. Hence, one would expect that the reactions of EX_2 (E = Ge or Sn) with trialkylsilanes (trialkylgermanes) exhibiting pronounced reducing properties will either follow the pathway giving rise to insertion products or proceed as one-electron oxidation of substrates to yield oxidative coupling or haloiodination products. To elucidate the real reaction mechanism, we

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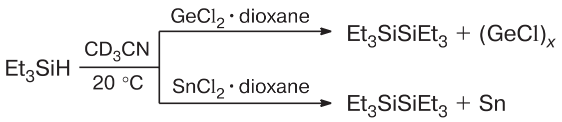
examined the reactions of dihalogermylenes, dihalostannylenes, and their complexes (EI_2, $ECl_2 \cdot$dioxane, and $(CO)_5W=ECl_2 \cdot THF$, where E = Ge or Sn) with triethylsilane and triethylgermane.

Results and Discussion

It appeared that the reactions of EI_2, $ECl_2 \cdot$dioxane, and $(CO)_5W=ECl_2 \cdot THF$ (E = Ge or Sn) with Et_3SiH and Et_3GeH did not afford the products of insertion of dichlorogermylene (dichlorostannylene) at the Si—H or Ge—H bond. However, the reactions of the $ECl_2 \cdot$dioxane complexes (E = Ge or Sn) or SnI_2 with triethylsilane (20 °C, CD_3CN, the reagent ratio was 1 : 1) gave rise to hexaethyldisilane in high yields. The reactions were accompanied by HCl liberation (as a gas) and reduction of $GeCl_2$ to yellow germanium subchlorides $(GeCl)_x$ or $SnCl_2$ to tin metal.



$$Et_3SiH + SnI_2 \xrightarrow{CD_3CN} Et_3SiSiEt_3$$

The reactions of $GeCl_2 \cdot$dioxane and SnI_2 with triethylgermane proceeded differently. Thus, the reaction of Et_3GeH with $GeCl_2 \cdot$dioxane performed under analogous conditions afforded Et_3GeCl accompanied by precipitation of $(GeCl)_x$, whereas the reaction of Et_3GeH with SnI_2 proceeded at room temperature very slowly and the reaction mixture contained Et_3GeI and Et_3GeH in a ratio of 2 : 1 even after 7 days.

$$Et_3GeH + GeCl_2 \cdot \text{dioxane} \xrightarrow{CD_3CN,\ 20\ ^{\circ}C} \longrightarrow Et_3GeCl + (GeCl)_x$$

$$Et_3GeH + SnI_2 \xrightarrow{CD_3CN} Et_3GeI$$

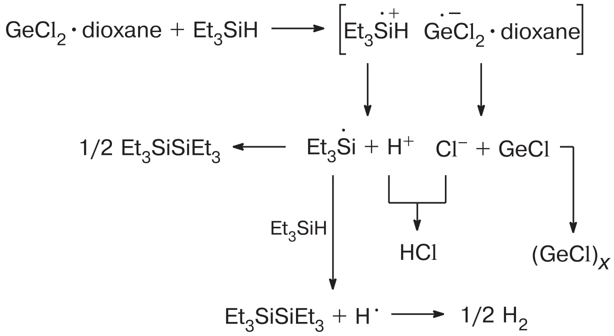
According to the results of the study,[14] the reactions of $GeCl_2 \cdot$dioxane with the $CpMo(CO)_2LGeCl_2H$ complexes (L = CO or PMe_3) in toluene at 20 °C proceeded analogously to form $CpMo(CO)_2LGeCl_3$, the reaction being much faster if L = PMe_3 than if L = CO. Unfortunately, the authors of the cited study[14] did not discuss the reaction mechanism and nothing was said as to the products of transformation of the $GeCl_2 \cdot$dioxane complex.

Unlike $GeCl_2 \cdot$dioxane, the $SnCl_2 \cdot$dioxane complex in a solution in CD_3CN did not react with Et_3GeH at 20 °C. Thus, only the starting Et_3GeH was isolated from the reaction mixture after 3 days. Diiodogermylene also did not react with triethylsilane or triethylgermane even upon ultrasonic irradiation of the reaction mixture for 10 h.

The influence of the reagent ratio and the solvent nature on the composition of the reaction products was studied using the reaction of Et_3SiH with $GeCl_2 \cdot$dioxane as an example. The reaction of Et_3SiH and $GeCl_2 \cdot$dioxane taken in a ratio of 1 : 1 in a medium of CD_3CN afforded exclusively $Et_3SiSiEt_3$, whereas the reaction mixture obtained with the use of the reagent ratio of 2 : 1 contained Et_3SiCl (32%) along with $Et_3SiSiEt_3$. At room temperature, the reaction of $GeCl_2 \cdot$dioxane with Et_3SiH in nonpolar benzene (instead of CD_3CN) did not take place.

The $(CO)_5W=ECl_2 \cdot THF$ complexes (E = Ge or Sn), in which dihalogermylenes (dihalostannylenes) exhibit more pronounced oxidizing ability,[15] vigorously reacted with two equivalents of $Et_3E'H$ (C_6D_6, 20 °C, 2—5 min). The reactions were accompanied by gas evolution (HCl) and reduction of E^{II} to metal (black powdered precipitate of Ge or Sn metal was obtained). The reaction of Et_3SiH with the $(CO)_5W=SnCl_2 \cdot THF$ complex afforded $Et_3SiSiEt_3$ as the only silicon-containing product. The reaction of Et_3SiH with $(CO)_5W=GeCl_2 \cdot THF$ gave rise to a mixture of Et_3SiCl and $Et_3SiSiEt_3$ in a ratio of 1 : 2. The reactions $(CO)_5W=ECl_2 \cdot THF$ (E = Ge or Sn) with triethylgermane produced Et_3GeCl, while hexaethyldigermane was not obtained. The reactions of $Et_3E'H$ (E′ = Si or Ge) with the $(CO)_5W=ECl_2 \cdot THF$ complexes (E = Si or Ge) were accompanied by destruction of the latter to give (according to the data from GLC-mass spectrometry) $W(CO)_6$ as one of the products.

The mechanism of the unusual oxidative dimerization of triethylsilane under the action of derivatives of Ge^{II} and Sn^{II} dihalides remains unclear. No signals belonging to the products of EX_2 insertion into the Si—H (Ge—H) bonds were observed in the studies of the reaction mixtures by ^1H NMR monitoring, which indicates that the formation of $Et_3SiSiEt_3$ is not associated with the secondary process of decomposition of these intermediates. At the same time, the formation of germanium subchlorides or germanium (tin) metal in the reactions of Et_3SiH with $ECl_2 \cdot$dioxane and $(CO)_5W=ECl_2 \cdot THF$ (E = Ge or Sn) indicates that the redox processes took place. In these processes, dichlorogermylene and dichlorostannylene complexes fulfilled an usual function serving as oxidizers. This is also evidenced by the low reduction potentials of $ECl_2 \cdot$dioxane and $(CO)_5W=ECl_2 \cdot THF$ (E = Ge or Sn).[13,15] The reactions discovered in the present study model oxidative electrochemical polymerization of diorganylsilanes R_2SiH_2 described in the literature.[16] The key step of the latter reaction involves one-electron oxidation of diorganylsilanes giving rise to the corresponding radical cations. Hence, based on the results of our study and the data published in the literature, the following mechanism of this reaction (as exemplified by the reaction of Et_3SiH with $GeCl_2 \cdot$dioxane) can be proposed:

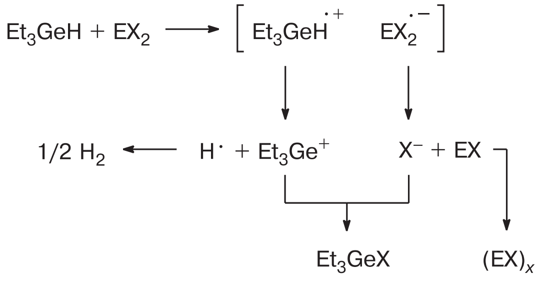


It should be noted that the existence of the $(Et_3SiH)^{\cdot+}$ radical cation[17] and $(GeCl_2 \cdot \text{dioxane})^{\cdot-}$ radical anion[14] has been proved previously.

In principle, the formation of $Et_3SiSiEt_3$ may also be associated with the bimolecular S_H2 reaction of the triethylsilyl radical with the starting silane analogously to that observed in the interactions of $Et_3Si^{\cdot}$ with dialkyl sulfides, dialkyl selenides, and bis(trimethylsilyl)mercury.[18] The possibility of the formation of the Si—Si bond *via* the direct attack of the triethylsilane radical cation on the starting silane must not be ruled out as well. It is this reaction that is the key step in the mechanism of electrochemical polymerization of diorganylsilanes.[16]

Other experimental facts can also be explained assuming that the reactions of Et_3E' with $ECl_2 \cdot$dioxane and $(CO)_5W{=}ECl_2 \cdot THF$ (E = Ge or Sn) involve the one-electron transfer. Thus, $Et_3E'H$ (E´ = Si or Ge) did not react with GeI_2 due, apparently, to the fact that the reduction potential of this germylene is in a much higher cathodic region as compared to the reduction potential of $GeCl_2 \cdot$dioxane ($E_{1/2}^{red}(GeI_2) = -0.99$ V and $E_{1/2}^{red}(GeCl_2 \cdot \text{dioxane}) = -0.41$ V with respect to Ag/AgCl/KCl (saturated)[13]).

The absence of $Et_3GeGeEt_3$ among the products of the reactions of Et_3GeH with $ECl_2 \cdot$dioxane, SnI_2, and $(CO)_5W{=}ECl_2 \cdot THF$ (E = Ge or Sn) can be attribtued to the fact that the fragmentation of the initially formed $Et_3GeH^{\cdot+}$ radical cation follows another pathway.



$EX_2 = ECl_2 \cdot$dioxane, SnI_2, $(CO)_5W{=}ECl_2 \cdot THF$ (E = Ge, Sn)

Oxidation of triethylsilane[19], triethylgermane,[20] and triethylstannane[21] under the action of such efficient oxidizing agents as transition metal salts MX_n was described in the literature. In all cases, Et_3EX (E = Si, Ge, or Sn) were formed and the salts were reduced to MX_{n-m} ($n - m = 1$ or 2) or free metal M.

To summarize dihalogermylenes (dihalostannylenes) and their complexes, unlike organylgermylenes, were not inserted at the Si—H and Ge—H bonds. The reactions of SnI_2, $ECl_2 \cdot$dioxane, and $(CO)_5W{=}ECl_2 \cdot THF$ (E = Ge or Sn) with $Et_3E'H$ (E´ = Si or Ge) occur as redox processes to form the products of oxidative coupling ($Et_3SiSiEt_3$) and/or haloiodination (Et_3SiX or Et_3GeX) of triethylsilane (triethylgermane) depending on the nature of the reagents.

Experimental

The ^1H NMR spectra were recorded on a Bruker AC 200 instrument (200 MHz). The GLC-mass spectra (EI, 70 eV) were measured on a Finnigan MAT INCOS instrument (RSL-200 column, 30 m × 0.25 mm). The solvents used in the reactions were dried over molecular sieves (CD_3CN) or sodium metal (C_6D_6). The $GeCl_2 \cdot$dioxane,[22] $SnCl_2 \cdot$dioxane,[23] $(CO)_5W{=}GeCl_2 \cdot THF$,[24] and $(CO)_5W{=}SnCl_2 \cdot THF$[25] complexes as well as GeI_2 [26] and SnI_2 [26] were prepared according to known procedures.

General procedure for the reactions. The EX_2 compound ($EX_2 = ECl_2 \cdot$dioxane, EI_2, or $(CO)_5W{=}ECl_2 \cdot THF$, where E = Ge or Sn) (0.661 mmol) was added to a solution of $Et_3E'H$ (E´ = Si or Ge) (0.661 mmol) in CD_3CN (C_6D_6) (0.5 mL) in an NMR tube under Ar. The course of the reactions was monitored by ^1H NMR spectroscopy (from the disappearance of the signal for the Si—H group (δ 3.63) in Et_3SiH and Ge—$\underline{H}$ group (δ 3.69) in Et_3GeH). ^1H NMR for $Et_3SiSiEt_3$ (CD_3CN), δ: 0.55 (m, 4 H, C$\underline{H}_2$—Si); 1.00 (m, 6 H, C$\underline{H}_3$). The reaction mixture was analyzed by GLC-mass spectrometry.

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