3. Irradiation of a doublet of doublets at δ 6.85 results in the appearance of singlets at δ 7.07 and 7.09 in the ^{1}H NMR spectrum of compound **4**.

It is noteworthy that free arylamine **1** (48%) is found in the reaction mixture. This probably accounts for the unique direction of the reaction studied, whose nature should be further investigated.

Experimental

IR spectra were recorded on a UR-20 instrument (film). ^{1}H NMR spectra were recorded on a Bruker AM-300 instrument (300.13 MHz) using $CDCl_3$ as the solvent and $SiMe_4$ as the internal standard. Mass spectra (EI, 70 eV) were obtained on a Hewlett Packard 5890A-5972A instrument. Chromatography was performed on columns filled silica gel LS 40/100 μm and Silpearl. TLC control was performed on Silufol UV-254 and UV-254/366 plates in the CH_2Cl_2—MeOH (95 : 5) system.

Dimethyldioxirane[7,8] and 2-(cyclopent-2-enyl)aniline hydrochloride (**2**)[6,9] were obtained by the described procedures.

A solution of DMDO (0.01 mol) in acetone (30 mL) was added with stirring at 0 °C to a solution of compound **2** (1.95 g, 0.01 mol) in acetone (10 mL). The solvent was evaporated *in vacuo*, and the residue was subjected to column chromatography to obtain compound **3** (0.41 g, 21%) and compound **4** (0.52 g, 27%).

3-Chloro-2-(cyclopent-2-enyl)aniline (3). Oil, R_f 0.81. IR, ν/cm^{-1}: 3460; 2960; 1620; 760. ^{1}H NMR ($CDCl_3$), δ: 1.75 (m, 2 H, CH_2); 2.35—2.60 (m, 2 H, CH_2); 3.48 (s, 2 H, NH_2); 4.00 (m, 1 H, CH); 5.8—6.0 (m, 2 H, CH=CH); 6.66 (d, 1 H, HC(6), J = 6.41 Hz); 6.86 (d, 1 H, HC(4), J = 7.71 Hz); 7.00 (dd, 1 H, HC(5), J_1 = 6.41 Hz, J_2 = 7.71 Hz). MS, *m/z*: 193 $[M]^+$. Calculated (%): C, 68.21; H, 6.25; N, 7.23; Cl, 18.30. $C_{11}H_{12}ClN$. Found (%): C, 67.76; H, 7.00; N, 7.22; Cl, 18.10.

6-Chloro-2-(cyclopent-2-enyl)aniline (4). Oil, R_f 0.63. IR, ν/cm^{-1}: 3460; 2940; 1615; 760. ^{1}H NMR ($CDCl_3$), δ: 1.80 (m, 2 H, CH_2); 2.35—2.60 (m, 2 H, CH_2); 3.42 (s, 2 H, NH_2); 4.05 (m, H, CH); 5.8—6.0 (m, 2 H, CH=CH); 6.85 (dd, 1 H, HC(4), J_1 = 6.34 Hz, J_2 = 7.58 Hz); 7.07 (d, 1 H, HC(3), J = 6.34 Hz); 7.09 (d, 1 H, HC(5), J = 7.58 Hz). MS, *m/z*: 193 $[M]^+$. Calculated (%): C, 68.21; H, 6.25; N, 7.23; Cl, 18.30. $C_{11}H_{12}ClN$. Found (%): C, 67.70; H, 7.08; N, 7.05; Cl, 18.13.

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Received November 21, 1997;
in revised form March 3, 1998

Synthesis of volatile alkoxygallium hydrides and study of their thermostability

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A method for the synthesis of alkoxygallium hydrides ($ROGaH_2$ and $(RO)_2GaH$, where R = Pr^i, Bu^t) was proposed. The method is based on the reaction of gallane GaH_3 with one or two equivalents of the corresponding alcohol. Thermolysis of these compounds was studied by differential thermogravimetry.

Key words: mono- and dialkoxygallium hydrides, isopropoxygallium dihydride, di(isopropoxy)gallium hydride, *tert*-butoxygallium dihydride, di(*tert*-butoxy)gallium hydride, synthesis, thermolysis.

Aluminum and gallium alkoxides $M(OR)_3$ (M = Al, Ga)[1] find use in the production of ceramic materials, active oxides, and oxide films in microelectronics obtained by epitaxial technology from the gas phase. In

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1655—1657, August, 1998.

1066-5285/98/4708-1612 $20.00

this case, it is important to have volatiles with low decomposition temperatures. The role of these compounds can be played by alkoxyhydrides of these metals of the type $HM(OR)_2$ and H_2MOR. Syntheses of similar aluminum derivatives are based on the reaction of ethereal solutions of AlH_3 with the calculated amounts of the corresponding alcohols;[2] in the case of $HAl(OR)_2$, they can also be obtained by direct synthesis from metallic Al and alcohol under hydrogen pressure.[3] Alkoxygallium hydrides are not known to date.

In the present work, we report the synthesis of H_2GaOR and $HGa(OR)_2$ (R = Pr^i, Bu^t) by the action of one or two equivalents of the corresponding alcohols on a solution of GaH_3 in THF. Gallium hydride was obtained by the reaction of $NaGaH_4$ with $GaCl_3$ in THF. A freshly prepared solution of $LiGaH_4$ can be used in this synthesis instead of $NaGaH_4$, because solid $LiGaH_4$ is unstable and difficult to store. The general scheme of preparation of alkoxygallium hydrides can be presented as follows:

$$MGaH_4 + GaCl_3 \longrightarrow GaH_3 \xrightarrow{n\,ROH} H_{3-n}Ga(OR)_n + n\,H_2,$$

R = Pr^i, Bu^t; M = Li, Na; n = 1, 2.

The reaction is carried out in THF. The corresponding amount of alcohol is added to a solution of GaH_3 when the first stage is over. The reactions with alcohols occur with noticeable rates and evolution of heat at −10 °C and are completed at room temperature. The second equivalent of an alcohol reacts considerably more slowly (heating to 50—60 °C for 2—3 h). The course of the reaction is easily monitored by measuring the volume of H_2 in a gas buret.

It is noteworthy that the purity of alkoxygallium hydrides (according to the determination of Ga and H) was the highest for the products obtained after removal of THF from the reaction mixture *in vacuo*. Subsequent distillations *in vacuo* (0.5—1.0 Torr) occurred without a distinct boiling temperature. The analysis of the fractions following distillation indicated a decrease in the content of Ga and hydride hydrogen, which is evidence for disproportionation and partial thermal decomposition of the reaction products. This phenomenon is especially pronounced in the case of distillation of H_2GaOR, where metallic gallium is formed in the distillation residue, and the content of H_2GaOR in the distillate decreases sharply. High-boiling fractions contain mainly $Ga(OR)_3$ with an insignificant admixture of a hydride.

The thermal behavior of alkoxygallium hydrides was studied by thermogravimetry. The complete thermal decomposition occurs at 250—300 °C. Dihydrides decompose to form Ga_2O_3, Ga, and RH according to the general scheme:

$$H_2GaOR \longrightarrow Ga + Ga_2O_3 + RH + H_2. \qquad (1)$$

Two thermoeffects are observed on the thermogram. One effect (at 90—120 °C) is evidently related to disproportionation of H_2GaOR and decomposition of GaH_3 to Ga and H_2.

$$2\,H_2GaOR \longrightarrow GaH_3 + HGa(OR)_2$$

Monohydrides decompose at 200—280 °C to give, along with Ga_2O_3, the corresponding hydrocarbons (RH) (products of the molecular decomposition), H_2, olefins, and oxo compounds (due to radical reactions).

$$2\,HGa(OR)_2 \longrightarrow Ga_2O_3 + 2\,RH + \underbrace{[R^{\cdot} + {}^{\cdot}OR]}_{\downarrow} \qquad (2)$$

H_2, RH, olefins, oxo products

Propane (85%), propylene (9%), hydrogen (5%), and liquid oxo products that have not been studied in detail were identified by GLC in the decomposition of $HGa(OPr^i)_2$ in the gas phase. It is noteworthy that the thermostability of alkoxygallium hydride derivatives is lower than that of the corresponding aluminum compounds (by 20—40 °C).

exo-Effects related to the weight loss due to the formation of gaseous products and Ga_2O_3 appear in the following temperature regions: for H_2GaOPr^i, the first step at 100—120 °C and the second step at 200—260 °C; for H_2GaOBu^t, the first step at 90—120 °C and the second step at 150—180 °C; for $HGa(OPr^i)_2$, the one-step at 210—295 °C; for $HGa(OBu^t)_2$, at 140—200 °C. Di(*tert*-butyl) derivatives are thermally less stable than the corresponding isopropyl compounds (by 50—70 °C). The weight loss in the thermal decomposition of $H_nGa(OR)_{3-n}$ corresponds satisfactorily to the calculations by Eqs. (1) and (2). For example, for the decomposition of $HGa(OPr^i)_2$ in a derivatograph in an argon medium, the experimental weight loss after heating of the sample to 380 °C was 55% and that calculated from Eq. (2) was 50%. We explain the difference of 5% as the result of removal of solid Ga_2O_3 particles as a dust.

Experimental

All experiments were carried out in an argon atmosphere. Tetrahydrofuran was purified by refluxing with KOH and distillation with addition of $NaAlH_4$. IR spectra were recorded on a UR-20 instrument. Thermogravimetric measurements were performed on a Q-gravitograph MOM instrument at 1000 °C with a rate of 5 deg min^{-1}. Gallium was determined by the trilonometric method, and active hydrogen was determined by the volumetric method after the decomposition of a weighed sample of a substance with 10% HCl. $NaGaH_4$ was synthesized by the previously described procedure.[4,5] $GaCl_3$ was obtained from metallic Ga and chlorine.[6]

Preparation of a solution of GaH_3 in THF. $NaGaH_4$ (6.04 g, 0.06 mol) and anhydrous THF (100 mL) were placed in an argon atmosphere in a three-neck flask with a magnetic stirrer. The solution was stirred at 20—40 °C for 1 h, and then a solution of $GaCl_3$ (3.25 g, 0.018 mol) in THF (50 mL) was added dropwise at −60 °C. The mixture was gradually heated to room temperature. The solution was filtered through a glass

filter into a calibrated Schlenk flask, and the precipitate was washed with THF (20 mL). According to the data of determination of hydride hydrogen, the solution contained 5.3 g of GaH_3 (0.078 mol) in 160 mL of THF.

Reaction of GaH_3 with isopropyl alcohol. *A. Ratio of reagents 1 : 1.* A solution of GaH_3 (1.32 g, 0.018 mol) in THF (40 mL) was introduced into a three-neck flask equipped with a magnetic stirrer, thermometer, addition funnel, and reflux condenser connected with a calibrated buret. Then a solution of Pr^iOH (1.09 g, 0.018 mol) in THF (20 mL) was poured slowly at −10 °C to the mixture; this resulted in a vigorous reaction. The temperature was raised to 20 °C, H_2 (401 mL, 0.018 mol) was released (0 °C, 760 Torr), and the reaction ceased. The THF was evaporated *in vacuo* (1 Torr), and the residue was heated at 50 °C to a constant weight. A viscous product (2.33 g, 98.3% with respect to H_2GaOPr^i) with m.p. 50—60 °C was obtained. IR, ν/cm^{-1}: 1913—1943. Found (%): Ga, 53.01; H, 1.50. Ratio Ga : H = 1 : 1.96. C_3H_9GaO. Calculated (%): Ga, 53.33; H, 1.54. The substance obtained (2 g) was distilled at 80—90 °C and 0.5 Torr. The product (1.4 g) with the ratio Ga : H = 1 : 1.85 was isolated.

B. Ratio of reagents 1 : 2. Pr^iOH (2.18 g, 0.036 mol) in THF (40 mL) was added to a solution of GaH_3 (1.32 g, 0.018 mol) in THF (40 mL) at −5 °C. The reaction rate was retarded after the addition of 1 equiv. alcohol. The reaction proceeded to completion upon heating the reaction mixture to boiling. H_2 (798 mL) was released. The solvent was distilled off *in vacuo*. The yield of the product was 3.4 g (99% with respect to $HGa(OPr^i)_2$). Found (%): Ga, 37.16; H, 0.58. Ratio Ga : H = 1 : 1.02. $C_6H_{15}GaO_2$. Calculated (%): Ga, 36.94; H, 0.53. The substance was distilled at 110—120 °C (1 Torr); purity with respect to H^- was 96% of the theoretical value.

Reaction of GaH_3 with *tert*-butyl alcohol. *A. Ratio of reagents 1 : 1.* A solution of Bu^tOH (1.33 g, 0.018 mol) in THF (20 mL) was added to a solution of GaH_3 (1.32 g, 0.018 mol) in THF (40 mL) for 20 min at −5 °C. The reaction mass was gradually heated to 40 °C to release 390 mL of H_2. The solvent was evaporated *in vacuo* (1.0 Torr) at 50 °C. A product in the form of a viscous semitransparent mass was obtained (2.65 g, 99%). Found (%): Ga, 47.86; H, 1.30. Ratio Ga : H = 1 : 1.96. $C_4H_{11}GaO$. Calculated (%): Ga, 48.17; H, 1.39. IR, ν/cm^{-1}: 1942. The substance was distilled *in vacuo* (1.0 Torr) at 80—90 °C with decomposition. The content of H^- in the distillate was 85% of the theoretical value.

B. Ratio of reagents 1 : 2. A solution of Bu^tOH (2.66 g, 0.036 mol) in THF (20 mL) was added dropwise at −5 °C to a solution of GaH_3 (1.32 g, 0.018 mol) in THF (40 mL). The reaction was retarded after the addition of 1 equiv. alcohol; the reaction mixture was heated to boiling, and H_2 (800 mL) was released. The solvent was removed *in vacuo*. A product in the form of a crystalline mass with m.p. 70—80 °C was obtained in 99.5% yield (4.11 g). IR, ν/cm^{-1}: 1942. Found (%): Ga, 31.91; H, 0.44. Ratio Ga : H = 1 : 0.96. $C_8H_{19}GaO_2$. Calculated (%): Ga, 32.17; H, 0.46. The substance was distilled at 80—90 °C and 1 Torr. Purity with respect to H^- was 93% of the theoretical value.

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Received December 5, 1997

Unusual exchange of functional groups at the silicon and metal atoms

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Reactions of α,ω-dichlorooligosilanes with metal hydroxides in the presence of pyridine results in the exchange of halogen and oxygen atoms and the formation of cyclic siloxyoligosilanes and pyridine complexes of metal halides. The metallosiloxane groups are not formed. A scheme for the transformations observed is proposed.

Key words: exchange reactions, metal complexes, polysilanes.

In all cases studied so far,[1] reactions of organochlorosiloxanes with metal hydroxides resulted in the formation of a metallosiloxane fragment according to the scheme

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1658—1659, August, 1998.