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1960

SovietRxiv

Abstract

Full Text

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ON THE PECULIARITIES OF THE EFFECT OF SILYL GROUPS

CHLORINATION OF ALKYLCHLOROSILICON HYDRIDES

The influence of the nature of silyl and germyl groups R_3M (M = Si, Ge), where R is an alkyl or aryl radical, on the chemical and physical properties of organosilicon and organogermanium compounds has been studied many times. Considerably less, or not at all, studied in this respect have been silyl and germyl groups containing hydrogen atoms or halogens $R_nX_{3-n}M$ (X = H, F, Cl, Br) ([1–10]). A systematic study of the effect of precisely these groups has enabled us to establish certain general features in the manifestation of their influence on the physical and chemical properties of a series of organic hydrides and halides of silicon and germanium ([5–8]). These features are connected first of all with the inductive influence of the silyl and germyl groups on the properties of both the nearest and the more distant bonds from silicon. At the same time it turned out that, in the radical and electrophilic reactions studied by us, a certain role is also played by the steric effect, noted also for the groups R_3M, of the atoms and groups bonded to silicon and germanium. And, finally, the specific character of the reactivity of the compounds studied by us, as well as of compounds containing R_3M groups, depends on the ability of Si and Ge to form coordination bonds (with participation of 3d-orbitals).

Table 1

"Competing" photochemical chlorination of alkylchlorosilicon hydrides with SO_2Cl_2 at 37–40°

	A. Cl_3SiH	A. CH_3SiHCl_2	A. $(CH_3)(C_2H_5)SiHCl$	A. $(CH_3)(C_2H_5)(Cl)SiH$	A. $(C_2H_5)(Cl_2)SiH$	A. $(C_2H_5)_2SiH_2$
Yield of chlorination products A, %	90	84	69	86	5	82
Yield of chlorination products B, %	0	0	Not more than 20	Not more than 8	0	55 $(C_2H_5)_2SiHCl$10 $(C_2H_5)_2SiCl_2$
Amount of A not entering into reaction, %	0	0	Not more than 20	Not more than 7	60	0
Amount of B not entering into reaction, %	50	89	57	69	85	0

Developing this line of work, in the present investigation we focused, first, on the photochemical chlorination of alkylsilane chlorides of the series: $(C_2H_5)_2SiH_2$, $(C_2H_5)_3SiH$, $(CH_3)(C_2H_5)_2SiH$, $(CH_3)(C_2H_5)(Cl)SiH$, $(C_2H_5)(Cl_2)SiH$, $(CH_3)(Cl)_2SiH$, and Cl_3SiH—with SO_2Cl_2 under conditions recently developed by Voronkov and Davydova ([11]). Second, we were interested in studying the influence of the electronegativity of chlorine atoms, as well as of alkyl and aryl groups, on the vibrational frequencies of Si—H bonds in certain mono- and dihydrides of silicon.

On the basis of the results we had obtained earlier concerning the directing and stabilizing effects of $R_n(X)_{3-n}Si$ groups, it could be expected that the transition from $(C_2H_5)_3SiH$ to Cl_3SiH should sharply decrease the rate of photochemical chlorination of the Si—H bonds of the indicated series of silicon hydrides-

compounds. As the data in Table 1 on the "competitive" chlorination of these silicon hydrides show, this was in fact the case.

Thus, the series of relative activity for these compounds fully corresponds to the series of increasing electron-withdrawing power of the silyl groups (see Table 2).

Table 2

Silicon hydride	X_c	ν_{Si-H}, cm^{-1}, exper.	ν_{Si-H}, cm^{-1}, calc.	Δ	Source
Cl_3SiH	2.235	2257	2260	−3	([8])
CH_3SiHCl_2	2.188	2214*	2212	+2	Our experim.
$C_2H_5SiHCl_2$	2.182	2204	2206	−2	([8])
$(CH_3)(C_2H_5)(Cl)SiH$	2.135	2161*	2158	+3	Our experim.
$(C_2H_5)_2(Cl)SiH$	2.082	2103*	2105	−2	» »
$(C_2H_5)_2SiH$	2.076	2098	2099	−1	([8])
$(C_2H_5)(C_6H_7)_2SiH$	2.078	2100*	2101	−1	Our experim.
$(CH_3)(CF_3CH_2CH_2)(Cl)SiH$	2.140	2170*	2173	−3	» »
$(F_3CCH_2CH_2)(CH_3)SiH_2$	2.121	2148*	2144	+4	» »
(*m*-$CF_3C_6H_4)(CH_3)SiH_2$	2.126	2152*	2149	+3	» »
(*n*-$CH_3C_6H_4)(CH_3)SiH_2$	2.115	2143*	2138	+5	» »
$(CH_2{=}CH)(CH_3)SiH_2$	2.117	2144*	2140	+4	» »
$(C_6H_5)_2SiH_2$	2.101	2130*	2124	+6	([7])
$(F_3CCH_2CH_2)_2SiH_2$	2.118	2139*	2141	−2	Our experim.

* The Raman spectra of the hydrides were recorded by N. S. Andreev, to whom we express our gratitude.

In analyzing these data, attention is also drawn to the fact that only Si–H bonds undergo chlorination, but not the C–H bonds of alkylchlorosilicon hydrides, although it is known ([11]) that under the same conditions the latter, in principle, can also be chlorinated. This difference in the behavior of Si–H and C–H bonds, as noted earlier ([12]), is associated with the specific nature of the Si–H bond and of the silicon atom itself, which, unlike carbon, possesses increased electrophilicity (participation of the 3*d*-orbitals of Si in the formation of the transition complex).

On the basis of these data one could have expected that photochemical radical chlorination of diethylsilane with SO_2Cl_2 should lead mainly to the formation of $(C_2H_5)_2SiHCl$. This could occur because of differences in the inductive and

steric effects of the chlorine*, hydrogen, and alkyl groups bonded to Si. Upon chlorination of $(C_2H_5)_2SiH_2$, only diethylchlorosilane was indeed obtained. We obtained an analogous result in the "competitive" chlorination of a mixture of $(C_2H_5)_2SiH_2$ and $(C_2H_5)_3SiH$.

The separation of the inductive, steric, and other effects of the group $R_{nX_{3-n}}Si$ from reactivity data is difficult. To some extent, data on the vibrational frequencies of Si–H bonds can help in solving this complex problem; as we showed earlier ([7,8]), these are sensitive to changes in the inductive effect of atoms and groups bonded to silicon. In our opinion, the most correct way to go from vibrational frequencies to electronegativities would be to use group electronegativities of silyl groups. One such empirical method was proposed in 1957 ([13]). On the basis of it, we recently derived ([14]) a simpler empirical relationship between the vibrational frequencies (ν) and the electronegativity values of silyl groups, namely $\nu = A \cdot X_c$, where ν is the valence vibrational frequency of the Si–H and Si–D bond, A is a constant equal to 1011 for silicon hydrides and 734 for silicon deuterides, and X_c is the effective electronegativity of the silyl group.

* The influence of chlorine atoms bonded to Si is manifested, evidently, not only in the fact that they strengthen the Si–H bond, but also in the fact that they strongly repel the chlorine atoms and ions conducting the reaction from the reaction center.

The electronegativity of the silyl group is regarded here as the sum of the effects of the three substituents bonded to Si. Using this equation and reliable literature data on the vibrational frequencies of Si–H bonds, as well as the data obtained by us for the hydrides studied, one can express quantitatively the influence of substituents, namely:

C_6H_{11}	iso-C_3H_7	C_2H_5	$C_3H_7 - C_6H_{13}$	CH_3,
(0.684)	(0.687)	(0.692)	(0.693)	(0.698)

n-$CH_3C_6H_4$,	C_6H_5	CH_2=CH–
(0.700)	(0.701)	(0.702)

$F_3CCH_2CH_2$ –	m-$CF_3C_6H_4$	$ClCH_2$	H
(0.706)	(0.711)	(0.717)	(0.717)

Br	Cl	F	CN	HF_2CF_2C–
(0.737)	(0.745)	(0.753)	(0.759)	(0.770)

The effective electronegativity of other silyl groups is determined by adding these values for the three substituents comprising the given silyl group. The vibrational frequencies of Si–H or Si–D bonds are readily found from the equation given above. It is seen from the data of Table 2 that the vibrational frequencies

of Si–H bonds calculated in this way agree quite well with the experimental values.

Experimental Part

1. **Di-(m-trifluoromethylphenyl)-silane** (I) was obtained by reaction of the Grignard reagent prepared from 98 g of m-bromobenzotrifluoride and 16.1 g of magnesium in ether with 13 g of dichlorosilane for 1 hour at −5°. After boiling the mixture (1 hour), decomposition with water, and the usual work-up, 25.8 g (63%) of (I) was obtained, b.p. 125–126° (12 mm), n_D^{20} 1.4806; d_4^{20} 1.2927. MR_D found 70.46; calculated 70.62.

	Found %:	C 51.93;	51.70;	H 3.18;	3.12;	F 35.82; 35.34
$C_{14}H_{10}F_6Si$.	Calculated %:	C 52.50;		H 3.15;		F 35.69

From the reaction products there was also isolated 0.7 g of m-$CF_3C_6H_4COOH$, b.p. 125–126° (12 mm), m.p. 104° (from alcohol), the formation of which in this case is difficult to explain. The valence vibrational frequency of the Si–H bond (ν_{Si-H}) in (I) is 2161 cm^{-1}.

2. **Di-p-tolylsilane** (II) was obtained under the conditions of experiment 1 from 119.7 g of p-bromotoluene, 19.44 g of magnesium, and 28.5 g of dichlorosilane in ether. Yield of (II) 46 g (74%), b.p. 137–139° (6 mm), n_D^{20} 1.5731; d_4^{20} 0.9836. MR_D found 71.14; calculated 70.44.

	Found %:	C 79.16;	79.20;	H 7.34;	7.43;	Si 13.30; 13.43
$C_{14}H_{16}Si$.	Calculated %:	C 79.19;		H 7.60;		Si 13.21

A small amount of p-$CH_3C_6H_4$—$C_6H_4CH_3$-p was also obtained, m.p. 120–123° (from alcohol). ν_{Si-H} in (II) is 2143 cm^{-1}.

3. **Bis(γ, γ, γ-trifluoropropyl)-silane** (III) was obtained from 38.3 g of 3-chloro-1,1,1-trifluoropropane, 12.2 g of magnesium, and 21.8 g of dichlorosilane in ether in an amount of 8.7 g (27%). B.p. (III) 45.5° (33 mm), n_D^{20} 1.3436; d_4^{20} 1.1928. MR_D found 39.78; calculated 40.24.

	Found %:	C 32.21;	32.08;	H 4.32;	4.55;	F 50.70; 51.03
$C_6H_{10}F_6Si$.	Calculated %:	C 32.14;		H 4.50;		F 50.84

ν_{Si-H} in (III) is 2152 cm^{-1}.

4. **Methyl-(m-trifluoromethyl)-phenylsilane** (IV) was obtained under the conditions of experiment 1 from 67.5 g of m-bromobenzotrifluoride,

11.9 g of magnesium, and 26 g of methylchlorosilane in ether in an amount of 32.5 g (57%). B.p. (IV) 43° (15 mm), n_D^{20} 1.4460; d_4^{20} 1.1042. MR_D found 45.91; calculated 46.08.

Found %:	C 50.61; 50.55;	H 4.92; 4.85;	F 28.53; 28.90
$C_8H_9SiF_3$. Calculated %:	C 50.51;	H 4.77;	F 29.97

ν_{Si-H} in (IV) is 2152 cm^{-1}.

5. **Methyl-*p*-tolylsilane (V)** was prepared from 96 g of *p*-bromotoluene, 17.01 g of magnesium, and 35 g of methylchlorosilane. Yield of (V) 36 g (60%). B.p. 63° (18 mm), n_D^{20} 1.5109; d_4^{20} 0.8817. MR_D found 46.28; calculated 45.99.

Found, %: C 70.77; 70.68; H 8.77; 8.73; Si 20.00; 20.00
$C_8H_{12}Si$. Calculated, %: C 70.53; H 8.88; Si 20.59

ν_{Si-H} for (V) is 2143 cm^{-1}.

In addition, 17.2 g of crystalline di-*p*-tolyl was isolated.

6. **Methyl-γ,γ,γ-trifluoropropylsilane (VI)** was obtained from 39.8 g of 3-chloro-1,1,1-trifluoropropane, 12.16 g of magnesium, and 25.3 g of methylchlorosilane in ether in an amount of 22 g (51%). B.p. 58.2° (759 mm), n_D^{20} 1.3408; d_4^{20} 0.9802. MR_D found 30.47; calculated 30.89.

Found, %: C 34.02; 33.73; H 6.33; 6.33; F 39.92; 40.40
$C_4H_9SiF_3$. Calculated, %: C 33.79; H 6.38; F 40.09

ν_{Si-H} for $(CH_3)(F_3CCH_2CH_2)SiH_2$ is 2148 cm^{-1}.

7. **Methylvinylsilane (VII).** To vinylmagnesium bromide, prepared from 40 g of vinyl bromide and 9.7 g of magnesium in tetrahydrofuran, a solution of 25.4 g of methylchlorosilane in tetrahydrofuran was added over the course of 1 hour. After completion of the reaction at room temperature, the solvent, together with the low-boiling products, was distilled off. 9 g (40%) of (VII) was isolated, b.p. 13.7° (757 mm), n_D^4 1.3920; d_4^4 0.6769; MR_D found 25.38; calculated 25.70. ν_{Si-H} for (VII) is 2144 cm^{-1}.

8. **"Competitive" chlorination of silicon hydrides.** Sulfuryl chloride and the silicon hydrides were introduced freshly distilled into the reaction. The molar ratio of reagents silicon hydride (A) : silicon hydride (B) : SO_2Cl_2 was 0.25 : 0.25 : 0.25, with the exception of the mixture $(C_2H_5)_3SiH$ and $(C_2H_5)_2SiH_2$, where A : B : SO_2Cl_2 was 0.2 : 0.2 : 0.4 mol. The reagents were charged into a quartz flask equipped with a thermometer and a reflux condenser. The mixture was heated to 37–40° under illumination with a PRK-4 mercury lamp. The end of the reaction was determined by cessation of gas evolution (3–5 h). SO_2 was separated from the product

mixture on a gas column; the residue was fractionated on an ordinary column. The results of the fractionation are presented in Table 1.

Energetic chlorination of 8 g (0.09 mol) of $(C_2H_5)_2SiH_2$ with 14 g of SO_2Cl_2 proceeded already on mixing the reagents. The only chlorination product was $(C_2H_5)_2SiHCl$ (41%). Diethyldichlorosilane was formed in a negligible amount.

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Academy of Sciences of the USSR

Received
17 II 1960

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Note: Figure translations are in progress. See original paper for figures.