[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Redistributions in Halogenosilanes and Alkylhalogenosilanes; Alkyliodochlorosilanes and Dimethylisocyanatochlorosilane

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Uncatalyzed equilibrium mixtures involve random distribution of alkyliodochlorosilanes and also in the system dimethyldichlorosilane, dimethylisocyanatochlorosilane and dimethyldiisocyanatosilane; in the absence of a catalyst the alkyl groups do not interchange. Random distribution applies to equilibrium mixtures of bromochlorosilanes or isocyanatochlorosilanes even when aluminum trichloride is present. Redistillation reactions have yielded the new compounds $MeSiCl_2I$, $MeSiClI_2$, Me_2SiClI, Et_2SiClI and $Me_2SiCl(NCO)$. Methyltrichlorosilane and methyltribromosilane furnished impure monomethylbromochlorosilanes, while ethylgermanium trichloride and ethylgermanium triiodide gave no stable intermediates. Tetrabromosilane and methylmagnesium bromide produced methyltribromosilane.

Calingaert and collaborators[1] first demonstrated that interchanges occur in many systems containing metal alkyls or organo(non)-metallic halides and showed a random distribution of the interchanged radicals or atoms in the products. We have reported random redistributions among numerous mixed halides of either carbon or silicon not containing alkyl groups.[2] In striking contrast to these findings, a non-random[3] redistribution occurs with methylchlorosilanes in the presence of aluminum chloride catalyst.

This present study of the redistributions of halogenosilanes sheds further light on the problem as a whole and includes some new compounds.

Experimental

A. **Preparations.**—Available starting materials included commercial alkylchlorosilanes and also alkyliodosilanes studied previously[4]; dimethyldiisocyanatosilane was again prepared from dimethyldichlorosilane[5] and AgNCO.

Alkyliodochlorosilanes.—In general the redistribution method was the best.[6] Heating 57 g. of methyltrichlorosilane and 104 g. of pure $MeSiI_3$ in a sealed Carius tube for 20 hr. at 300° yielded, upon distillation, 35 g. of methyltrichlorosilane, b.p. 66°, 44 g. of methyldichloroiodosilane, b.p. 115–120°, 44 g. of methylchlorodiiodosilane, b.p. 171–177°, and 29 g. of methyltriiodosilane, boiling at about 227°; upon at least two redistillations, 16 g. of pure methyldichloroiodosilane and 7.5 g. of pure methylchlorodiiodosilane resulted, as in Table I. All the iodochlorosilanes herein were redistilled over copper powder in equipment with ground joints. Twenty hours at 300° was insufficient for equilibrium, but this run and another not listed showed that the reaction rates were about 3%/hr. at this temperature.

Essentially random distribution occurred when 5.2 g. of diethyldichlorosilane and 11.2 g. of diethyldiiodosilane were heated in a sealed tube for 10 hr. at 400°; distillation yielded 3.40 g. of diethyldichlorosilane, 7.93 g. of diethylchloroiodosilane, b.p. chiefly 172–179°, and 5.52 g. of diethyldiiodosilane. After combination with material from the aniline method above, three distillations gave a 2.5-ml. center cut (Table I).

In an electric furnace 45 cm. long, a three-hour passage and a later two-hour repassage of 9.7 g. of dimethyldichlorosilane and 21.3 g. of pure dimethyldiiodosilane through a Pyrex tube, at an average temperature of 450°, yielded 4.0 g. of dimethyldichlorosilane, 9.9 g. of dimethylchloroiodosilane and 9.1 g. of dimethyldiiodosilane (Table I).

Dimethylisocyanatochlorosilane.—Equal volumes of dimethyldichlorosilane and of dimethyldiisocyanatosilane, after heating 7 hr. in an autoclave at 370°, furnished 6.7 g. of dimethyldichlorosilane, 11.4 g. of dimethylchloroisocyanatosilane and 5.0 g. of dimethyldiisocyanatosilane; a small higher-boiling residue containing chlorine was approximately $Me_2Si(NCO)\text{-}O\text{-}Si(Cl)Me_2$, boiling at approximately 170°. Table I lists the properties of the five new alkylhalogenosilanes.

Other redistributions included that of nearly equal weights of ethylgermanium trichloride and ethylgermanium triiodide, which failed to produce any stable compound such as $EtGeCl_2I$, when heated for one hour at 310°, and later distilled at 10 mm.; the redistribution of methyltrichlorosilane and methyltribromosilane on a large scale at 450° yielded a probably fair grade methyldichlorobromosilane, b.p. 87.4°, of density 1.61 at 30°, and of neutralization equivalent 66, and also yielded a strongly contaminated methylchlorodibromosilane, b.p. 107°, of density 2.02 at 20, and of neutralization equivalent only 69. This is not the proper mode of preparation.

One mole of methylmagnesium bromide when added to 400 g. of tetrabromosilane in ether yielded at least 160 g. of methyltribromosilane, with little or no dimethyldibromosilane.[7]

Properties and Analyses of New Compounds.—All five of the new compounds are colorless, mobile liquids when pure; the alkyliodochlorosilanes hydrolyze more readily than alkylchlorosilanes, but less readily than alkyliodosilanes; dimethylisocyanatochlorosilane hydrolyzes rapidly. In the analysis of the isocyanate, 2.5 hr. in neutral 100% ethanol destroyed the isocyanate completely,[8] so then the chloride could be titrated with base.

B. **Redistribution Experiments.**—Using a sealed tube, an autoclave, or an open tube,[2] the sample was heated until equilibrium resulted; after cooling, the sample was placed in a preweighed distilling unit and the unit reweighed; the unit held a male and a female 10/30 ground-glass joint for accepting a receiver and a thermometer, respectively. To illustrate operations, diethyldichlorosilane, which boils at 129°, was distilled off up to 152°, and the system weighed to a centigram; next diethylchloroiodosilane was distilled up to 199°, and the system reweighed, the pure compound boiling at 176.5°; diethyldiiodosilane was the residue. All distillation columns in this paper were unpacked, 6 mm. o.d. and 300 mm. long, with five theoretical plates. Table II lists the results; the methods of calculating mole percentages of individual compounds assuming random distribution follow the published methods.[1]

Discussion

Table II shows that the uncatalyzed redistribution of methyliodochlorosilanes or of dimethylisocyanatochlorosilane follows random distribution; the methyl groups are not mobile, but slow

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[1] G. Calingaert and others, THIS JOURNAL, **61**, 2748, 2755, 2758, 3300 (1939); **62**, 1099, 1104 (1940).

[2] G. S. Forbes and H. H. Anderson, *ibid.*, **66**, 931 (1944); **67**, 1911 (1945); H. H. Anderson, *ibid.*, **66**, 934 (1944); **72**, 2091 (1950).

[3] R. O. Sauer and E. M. Hadsell, *ibid.*, **70**, 3590 (1948); P. D. Zemany and F. P. Price, *ibid.*, **70**, 4222 (1948).

[4] H. H. Anderson, D. L. Seaton and R. P. T. Rudnicki, *ibid.*, **73** 2144 (1951); H. H. Anderson, *ibid.*, **73**, 2351 (1951).

[5] G. S. Forbes and H. H. Anderson, *ibid.*, **70**, 1222 (1948).

[6] Me_2SiI_2 and dry $SbCl_3$ yielded only Me_2SiCl_2 in a rapid reaction; dry $HgCl_2$ reacted easily, giving 2 grams of Me_2SiCl_2 for every gram of Me_2SiClI when heated. Simultaneous passage of anhydrous HCl and HI into a solution of diethyldianilinosilane gave Et_2SiCl_2 and Et_2SiI_2. One hundred grams of Et_2SiCl_2 was treated with enough aniline to replace *one* chlorine, the anilinium chloride filtered and then anhydrous HI passed into the filtrate; 45 g. of Et_2SiCl_2, 15 g. of Et_2SiClI and 25 g. of Et_2SiI_2 resulted in the benzene solution.

[7] C. J. Wilkins, N. P. H. Brown and A. D. Stevens, *J. Chem. Soc.*, 163 (1950). These authors report no reaction.

[8] G. S. Forbes and H. H. Anderson, THIS JOURNAL, **69**, 1241 (1947).

TABLE I

PROPERTIES OF NEW COMPOUNDS

Compound[a]	B.p., °C.	d^{20}_4	Mol. wt. (Dumas) Calcd.	Mol. wt. (Dumas) Found	Neut. equiv., g. (to NaOH in EtOH) Calcd.	Neut. equiv., g. (to NaOH in EtOH) Found	Iodine, % Calcd.	Iodine, % Found[b]
$MeSiCl_2I$[c]	116.5	1.903	240.9	246	80.3	80.2, 79.9	52.7	52.3, 52.1
$MeSiClI_2$[d]	173	2.451	332.4	321	110.8	110.4, 110.2	76.5	76.2, 75.5
Me_2SiClI	118.5	1.689	220.5	230	110.3	109.4, 109.2	57.5	56.7, 57.3
Et_2SiClI	176.5	1.563	248.6	238	124.3	124.3, 124.5	51.0	50.5
$Me_2SiCl(NCO)$[e]	103.3	1.075	135.6	133	67.8	....	26.2	26.1, 26.5[f]

[a] Compounds collected over b.p. range of one degree or less. [b] Liberated using ferric nitrate, extracting into CCl_4, then titrating with thiosulfate. [c] n^{20} is 1.504_4; R is 37.5. [d] n^{20} is 1.600; R is 46.4. [e] n^{20} is 1.414_0; R is 31.53. [f] % chlorine.

TABLE II

REDISTILLATION OF ALKYLHALOGENOLSILANES

Initial reactants	Mol. fract., Cl	Treatment hr.	Treatment °C.	Products, in mole per cent.	A obsd. calcd.		B obsd. calcd.		C obsd. calcd.		D obsd. calcd.		E obsd. calcd.
							Without a catalyst						
$MeSiCl_2I$	0.667	0.5	460	Cl_3	27	Cl_2I	48	ClI_2	24	I_3	2	.....	..
					29.6		44.4		22.2		3.7		
$MeSiClI_2$	.333	0.5	460	Cl_3	6	Cl_2I	24	ClI_2	39	I_3	32	.....	..
					3.7		22.2		44.4		29.6		
Me_2SiCl_2,	.52	[a]	480	Cl_2	29	ClI	44	I_2	27	......	..	.....	..
Me_2SiI_2					27		50		23				
Et_2SiCl_2,	.53	10	400	Cl_2	31	ClI	46	I_2	23	......	..	.....	..
Et_2SiI_2					28.8		49.8		21.5				
$Me_2Si(NCO)_2$	.545	7	370	Cl_2	30	$Cl(NCO)$	49	$(NCO)_2$	20	......	..	.....	..
Me_2SiCl_2					29.7		49.6		20.7				
							With $KAlCl_4$ catalyst						
$SiCl_4$,	.50	2	310	Cl_4	8	$Cl_3(NCO)$	23.5	$Cl_2(NCO)_2$	35	$Cl(NCO)_3$	23	$(NCO)_4$	10.5
$Si(NCO)_4$					6.3		25		37.5		25		6.3
$SiCl_4$,	.494	2	300	Cl_4	8	Cl_3Br	23	Cl_2Br_2	34	$ClBr_3$	26	Br_4	8
$SiBr_4$					6.0		24.6		37.5		25.6		6.6

[a] Three-hr. passage, then two-hr. passage.

down the rate of reaction approximately a thousand-fold, as compared with bromochlorosilanes; the presence of $KAlCl_4$ does not change the random nature of redistribution in bromochlorosilanes or isocyanatochlorosilanes, such as previously observed in the absence of a catalyst.[2]

Thus these results are in contrast with those obtained when methylchlorosilanes were brought to equilibrium with aluminum chloride.[3]

In the series tetramethylsilane, trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane and tetrachlorosilane there is non-random distribution,[3] also a non-linear increase in boiling points, and probably an appreciable dipole moment in the dichloro compound; all this appears to be in contrast with the regular increases in boiling point (also with random distribution) of the four new series, listed in Table III.

TABLE III

BOILING POINTS IN SEVERAL SERIES OF ALKYLHALOGENOSILANES

Compounds	B.p., °C.	Δ, °C.	Compounds	B.p., °C.	Δ, °C.
$MeSiCl_3$	65.7	50.8	Me_2SiCl_2	70.0	48.5
$MeSiCl_2I$	116.5	56.5	Me_2SiClI	118.5	51.5
$MeSiClI_2$	173	56.0	Me_2SiI_2	170	
$MeSiI_3$	229				
Me_2SiCl_2	70.0	33.3	Et_2SiCl_2	129	47.5
$Me_2SiCl(NCO)$	103.3	35.9	Et_2SiClI	176.5	44.5
$Me_2Si(NCO)_2$	139.2		Et_2SiI_2	221	

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