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REDISTRIBUTION STUDIES AND PREPARATION OF CHLOROBROMODISILANES *

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Summary

Distribution reactions between Si_2Cl_6 and Si_2Br_6 yield all mixed chlorobromodisilanes of the form $\text{Si}_2\text{Cl}_x\text{Br}_{6-x}$. Further redistributions prevent the separation of the mixed compounds by vacuum distillation. A direct preparation of 1,1,1-tribromo-2,2,2-trichlorodisilane via 1,1,1-triphenyl-2,2,2-trichlorodisilane by means of HBr/AlBr_3 yields a pure compound.

Introduction

Mixed halodisilanes $\text{Si}_2\text{Cl}_x\text{Br}_{6-x}$ are not well known, because of the lack of appropriate synthetic routes. Only one member of this class, $\text{Si}_2\text{Cl}_4\text{Br}_2$ could be obtained as a colorless liquid as a by-product of the reaction between intermediate SiCl_2 and Br_2 , described by Schenk and Bloching [1].

Two in principle different routes are possible for the synthesis of such disilane derivatives. The first comprises redistribution reactions. We have investigated the reaction between Si_2Cl_6 and Si_2Br_6 in detail. All mixed chlorobromodisilanes are shown to be formed in this redistribution reaction, but subsequent rearrangements between the different derivatives do not allow separation of pure compounds by fractional distillation.

The second route to form mixed halodisilanes starts with partially phenylated chlorodisilanes. Gilman has developed synthetic procedures for large scale synthesis of organohalodisilanes [10,11]. Arylchlorodisilanes are suitable precursors for bromochlorodisilanes by Si-phenyl-cleavage reactions using HBr in presence of AlBr_3 as a catalyst. This route makes possible the synthesis of pure bromochlorodisilanes, but in our experience, we have seen that pure compounds also undergo redistribution reactions on being heated for longer periods of time.

* In honour of Professor Henry Gilman for his many years of outstanding research and teaching in the field of organometallic chemistry.

Redistribution reactions

In redistribution reactions two (or more) kinds of exchangeable substituents change sites with each other on one (or more) kinds of polyfunctional central moieties. If allowed to proceed a sufficiently long time at a proper reaction temperature, these reactions generally reach equilibrium. Redistribution reactions originally served as a synthetic method for the preparation of certain classes of compounds. There is a large body of information about redistribution of labile ligands, such as halogens and pseudohalogens, on tetravalent silicon [2,3]. These labile ligands are most easily redistributed and, in fact, these redistributions often occur spontaneously upon mixing the appropriate compounds.

The redistribution of halogens and pseudohalogens has been investigated previously by H.H. Anderson [4,5]. These exchanges occur very rapidly at 600–700°C, but also at lower temperatures, with longer reaction times, in sealed tubes [4]. However, most of the mixed halomonosilanes are sufficiently stable to allow isolation by rapid distillation. The recent quantitative studies by Moedritzer and Van Wazer [6] have shown that rapid redistribution of a variety of halogens with one another occur by heating in sealed ampoules at 100–150°C. In comparison with the large body of information about redistribution of monosilanes, there are only few papers, cited in the comprehensive review by K. Moedritzer [2], in which the redistribution reactions of disilane moieties are described. These disilanes, for example with $-\text{N}(\text{CH}_3)_2$, $-\text{C}_2\text{H}_5$, $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{Cl}$, $-\text{H}$ ligands, form mono- and oligosilanes when they are heated with a catalyst. In most cases, cleavage of the Si–Si bond takes place. However, it is possible to synthesize mixtures of mixed substituted fluorodisilanes which also contain bromo and chloro ligands by heating a mixture of the corresponding disilanes, as shown in some ^{19}F NMR investigations by Johannesen [7]. This paper primarily reports NMR data but the reactions have not been examined in detail.

Quantitative studies on redistribution equilibria were made only on tetravalent silicon moieties. With respect to recent work of Calingaert [8], K. Moedritzer [2,9] developed a statistical method to calculate the equilibrium concentration of a compound at any overall composition of the system. Halogen exchange on silicon was found to depend on these statistic principles called random redistribution.

In our redistribution studies we tried to examine whether or not these generalizations are transferable to disilanes. For the calculation of the "random mixture" we used the statistical method cited above.

Experimental and results

NMR studies

The preparation of mixed chlorobromomonosilanes described by Forbes and Anderson [4], has been used as a model for our redistribution studies. These authors obtained all mixed chlorobromosilanes by heating a mixture of SiCl_4 and SiBr_4 at 140°C for seventy hours in a sealed tube. Thus, we heated an equimolar mixture of Si_2Cl_6 and SiBr_4 (dissolved in C_6D_6) in a thick-walled NMR tube for 35 days at 100°C. By ^{29}Si NMR measurements we detected small amounts of $\text{Si}_2\text{Cl}_3\text{Br}_3$ and SiCl_2Br_2 . After longer reaction times, for example 63 or 90 days, no further changes in the ^{29}Si NMR spectra were observed. Only a partial bromi-

nation of Si_2Cl_6 and a partial chlorination of SiBr_4 took place.

A second experiment with Si_2Br_6 and SiCl_4 confirmed the slow and partial exchange of halogens between mono- and disilanes without cleavage of the Si—Si bond.

In contrast to the slow halogen exchange between mono- and disilanes, the reaction between Si_2Cl_6 and Si_2Br_6 led to rapid halogen exchange. All mixed halo-disilanes of the form $\text{Si}_2\text{Cl}_x\text{Br}_{6-x}$ could be detected by ^{29}Si NMR measurements when a mixture of Si_2Cl_6 and Si_2Br_6 (molar ratio 1 : 1) was heated at 100°C for three weeks in a sealed tube. The resulting spectrum is shown in Fig. 1. With respect to ^{29}Si NMR spectra of Si_2Cl_6 , Si_2Br_6 and $\text{Si}_2\text{Cl}_3\text{Br}_3$, all ^{29}Si NMR signals of the reaction mixture could be assigned on the basis of the effect of step by step replacement of one halogen by the other on NMR chemical shift (see Table 1). The ^{29}Si NMR signal intensities allow only approximate determinations of the molar concentrations at the equilibrium state because of nonlinear dependence of signal intensities on molar concentration. Thus the quadrupole moments of the halogens and different relaxation times effect a different line broadening of the NMR peaks, which are partially superimposed (see Fig. 1).

Raman studies

A better quantitative examination of the equilibrium mixture was obtained using Raman spectroscopy. This technique does not require any solvent, so we were able to investigate the reaction between Si_2Cl_6 and Si_2Br_6 in the absence of a solvent. Thus, an equimolar mixture of Si_2Cl_6 and Si_2Br_6 was heated at 100°C in a sealed tube. The tube was periodically cooled in liquid nitrogen in order to give a homogeneous mixture for the subsequent Raman measurements.

For detection of molar concentrations, we employed measurements on the most intense signals corresponding to a combined (SiSi)/(SiHal) stretching motion. This band shows a characteristic shift $\Delta\nu = -21\text{ cm}^{-1}$, upon exchange of chlorine with bromine. Because measurements of the absolute Raman intensi-

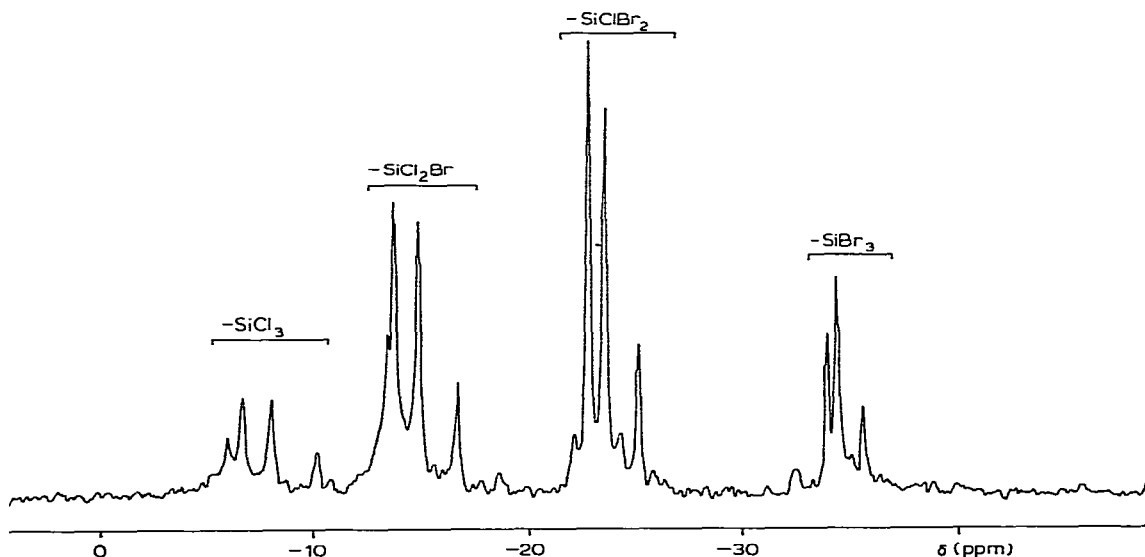


Fig. 1. ^{29}Si NMR spectra of a mixture of Si_2Cl_6 and Si_2Br_6 after reaction.

TABLE 1

²⁹Si NMR CHEMICAL SHIFTS OF MIXED HALOGENODISILANES (ppm, relative to external TMS)

Halogenodisilane	δ (ppm) (A)	δ (ppm) (B)
(A) (B)		
Cl ₃ Si—SiCl ₃	-6.169	-6.169
Cl ₃ Si—SiCl ₂ Br	-6.786	-13.531
Cl ₃ Si—SiClBr ₂	-8.143	-22.650
Cl ₃ Si—SiBr ₃	-10.200	-34.260
Cl ₂ BrSi—SiCl ₂ Br	-13.860	-13.860
Cl ₂ BrSi—SiClBr ₂	-14.929	-22.908
Cl ₂ BrSi—SiBr ₃	-16.739	-33.930
ClBr ₂ Si—SiClBr ₂	-23.690	-23.690
ClBr ₂ Si—SiBr ₃	-25.211	-34.342
Br ₃ Si—SiBr ₃	-35.575	-35.575

ties are very complicated, we used the intensities of Si₂Cl₆ and Si₂Br₆ for the calculation of the unknown standard intensities of the mixed chlorobromodisilanes by linear interpolation. Figure 2 shows the results of our measurements. The reaction mixture comes to equilibrium within 60–70 hours, and the rate curves show only small deviations from randomness, calculated by the statistical method discussed by K. Moedritzer [2].

Synthesis of mixed compounds

We tried to synthesize the mixed halodisilanes by equilibration of Si₂Cl₆ and Si₂Br₆ followed by separation through distillation. We used a 2 × 20 cm Vigreux column. By distillation under reduced pressure (40–80°C, 20–1 Torr), the mixed halodisilanes could be concentrated, but pure compounds could not be obtained. It is highly probable that rearrangement occurs during distillation.

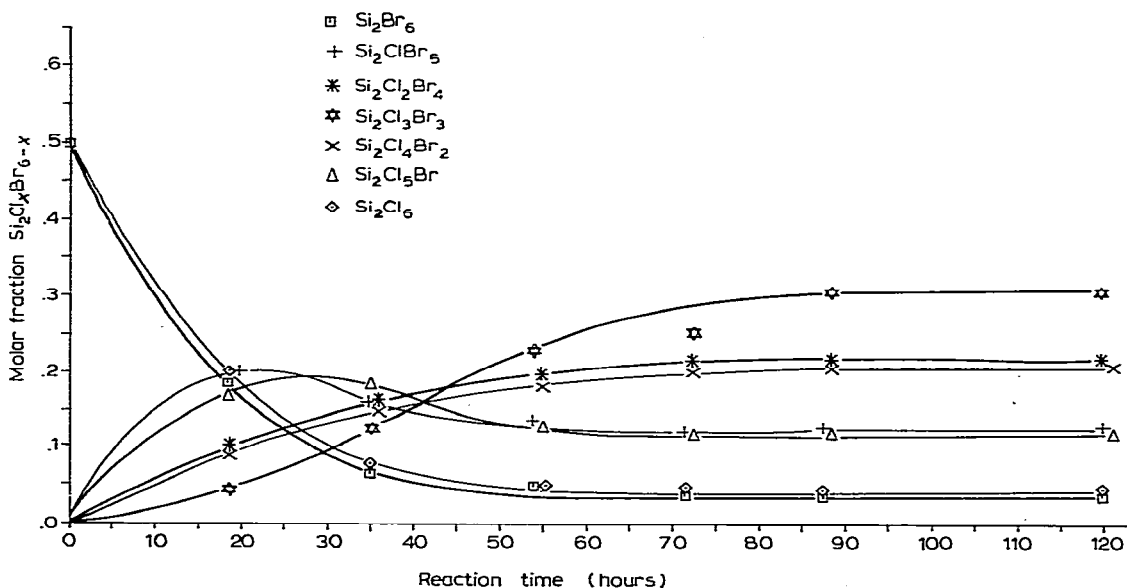


Fig. 2. Concentration of mixed chlorobromosilanes versus reaction time. Reaction temperature: 100°C, concentrations were calculated from Raman intensities.

This can be confirmed by the rapid redistribution of the pure compound $\text{Si}_2\text{Cl}_3\text{Br}_3$ described below upon heating at 100°C . Also a second distillation of the concentrated compounds produced a mixture of all mixed halodisilanes instead of further purification.

The redistribution experiments suggested other synthetic routes for the preparation of mixed chlorobromodisilanes. The relatively high temperature for the isolation of chlorobromodisilanes by vacuum distillation from the redistribution mixture seems to be the source of further redistribution reactions and the difficulties in the isolation of the compounds. Therefore, a synthetic route had to be found which did not use higher temperatures. The cleavage of phenyl groups from Si atoms by means of hydrogen halide in presence of aluminium halide as a catalyst seems to be a convenient method. Because it is easier to cleave with HBr/AlBr_3 , and SiCl linkages are not attacked by HBr , suitable starting materials were phenylchlorodisilanes. We used the readily preparable 1,1,1-triphenyltrichlorodisilane. Reaction of this compound with HBr/AlBr_3 yields in a simple way the expected 1,1,1-tribromo-2,2,2-trichlorodisilane. For separation of this compound from the solvent and for all purification procedures (sublimation), a low temperature is necessary to avoid redistribution reactions. Thus, 1-chloropentabromodisilane, prepared from 1-chloropentaphenyldisilane [10] in the same manner underwent redistribution during purification by sublimation at 40°C (0.01 Torr), because lower temperatures could not be used.

1,1,1-Tribromo-2,2,2-trichlorodisilane

In a 250 ml three-necked flask, fitted with a KPG-stirrer, a gas inlet tube and a reflux condenser, was placed 10 g (0.025 mol) of 1,1,1-triphenyl-2,2,2-trichlorodisilane *, after the flask had been swept with dry, oxygen-free nitrogen. To this was added a catalytic amount (0.2 g) of AlBr_3 and 150 ml of dry benzene. Hydrogen bromide from a cylinder provided with a needle valve and a safety tube was passed through a drying tube filled with P_2O_5 . The carefully dried gas was then passed through the stirred reaction mixture at a rate of 2 to 4 bubbles per second. Slight warming indicates the start of the cleavage reaction. After about one hour, the solution developed a brown colour. The reaction was completed, when the mixture cooled down. Solvent was distilled from the resulting solution under reduced pressure.

The crude product was separated from the catalyst and by-products by sublimation at room temperature (0.05 Torr) into an evaporated bulb, cooled with liquid nitrogen, to give a colorless solid, melting at $54\text{--}56^\circ\text{C}$ (uncorr.). The yield of the pure product was 8.2 g (82%). Analysis: Found: Si, 14.1; Cl, 26.1; Br, 59.9. Calcd. for $\text{Si}_2\text{Br}_3\text{Cl}_3$: Si, 13.9; Cl, 26.4; Br, 59.6%. ^{29}Si NMR chemical shifts: (to external TMS, 30% C_6D_6): $\delta(-\text{SiCl}_3)$: -10.200 ppm, $\delta(-\text{SiBr}_3)$: -34.260 ppm IR, Raman spectra: see Table 2. Mass spectrum: The mass spectrum of $\text{Si}_2\text{Cl}_3\text{Br}_3$, recorded with a JEOL JMS-Q10 at an ionization energy of 25 volts, does not show the parent peak. All fragments of the form $-\text{SiCl}_x\text{Br}_{3-x}$, which were detected are not specific for the substance being mea-

* 1,1,1-Triphenyl-2,2,2-trichlorodisilane was prepared by a method developed by H. Gilman [11]. We purified the crude product by sublimation (130°C , 0.01 Torr).

TABLE 2
VIBRATIONAL SPECTRA OF $\text{Si}_2\text{Cl}_3\text{Br}_3$ (cm^{-1})

Raman	IR	Assignment	Species
590vw	595vs	$\nu(\text{SiSi})$	A_1
410vw	415s	$\nu_s(\text{SiCl}_3)$	
275s	275s	$\nu_s(\text{SiBr}_3)$	
188s	197s	$\delta_s(\text{SiCl}_3)$	
97s	102m	$\delta_s(\text{SiBr}_3)$	
590vw	595vs	$\nu_{as}(\text{SiCl}_3)$	E
480vw	485s	$\nu_{as}(\text{SiBr}_3)$	
188s	197s	$\rho(\text{SiCl}_3)$	
130m	136m	$\delta_{as}(\text{SiCl}_3)$	
97s	102m	$\delta_{as}(\text{SiBr}_3)$	
63 (calcd.)	63 (calcd.)	$\rho(\text{SiBr}_3)$	

Intensities — vw = very weak; w = weak; m = medium; s = strong; vs = very strong.

sured. It is highly probable that rearrangement takes place during acquisition of the mass spectra.

^{29}Si NMR measurements were carried out using a Bruker WH-90 NMR spectrometer, infrared spectra in the range $300\text{--}800\text{ cm}^{-1}$ were measured with a Perkin-Elmer 325 spectrometer, and the $50\text{--}300\text{ cm}^{-1}$ region was examined with a Beckman 725 Fourier spectrophotometer. The spectra were recorded using Nujol mulls. Raman spectra were recorded with a Spex Ramalog (25 mW HeNe source).

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