PREPARATION AND PROPERTIES OF METHOXY-TRIFLUOROSILANE, AND STUDY OF ITS REACTIONS WITH BORON TRIHALIDES

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Abstract – MeOSiF₃ is formed when gaseous MeOSiCl₃ is passed through SbF₃; its reaction with BBr₃ provides a convenient preparation of F₃SiBr. Similarly BF₃ and BCl₃ yield SiF₄ and F₃SiCl respectively. The other product in these reactions is MeOBX₂ (X = Br, F, Cl respectively), but the methoxy boron dibromide decomposes to give methyl bromide and boron oxybromides.

INTRODUCTION

TRIFLUOROSILYL bromide has considerable potential as a starting material for the syntheses of trifluorosilyl derivatives [1, 2]; in an attempt to devise an efficient synthesis of this compound we have investigated the reaction sequence:

> $SiCl_4 + MeOH \rightarrow MeOSiCl_3 + HCl$ $MeOSiCl_3 + SbF_3 \rightarrow MeOSiF_3 + SbF_xCl_{3-x}$ $MeOSiF_3 + BBr_3 \rightarrow F_3SiBr + MeOBBr_2.$

Methoxytrichlorosilane was prepared by the addition of anhydrous methanol to a solution of silicon tetrachloride in diethyl ether[3].

An NMR spectrum of a solution in cyclohexane indicated some disproportionation into $Cl_2Si(OMe)_2$, $ClSi(OMe)_3$ and (presumably) $SiCl_4$. The chemical shifts were consistent with those assigned[4] to the methoxy chlorosilanes in thermally equilibrated mixtures of $SiCl_4$ and $Si(OMe)_4$. The methoxytrichlorosilane was converted into methoxytrifluorosilane by distillation through a column packed with dry antimony trifluoride (without a catalyst); a similar procedure has been found successful for ethoxytrifluorosilane [5]. On the other hand no methoxytrifluorosilane was formed when KHF_2 was used as the fluorinating agent. The previously unreported methoxytrifluorosilane was characterised by ¹H and ¹⁹F NMR, i.r. and mass spectroscopy, and by determination of the vapour density. A silicon analysis was performed by quantitative conversion to silicon tetrafluoride using antimony trifluoride with an antimony pentachloride catalyst.

We first attempted to prepare trifluorosilyl halides by cleavage of the Si—O bond in MeOSiF₃ with hydrogen halides. No reaction was observed, however, with hydrogen bromide or iodide in either the vapour or liquid phases. In the

^{1.} W. Airey and G. M. Sheldrick, J. chem. Soc. A, 2865 (1969).

^{2.} W. Airey and G. M. Sheldrick, J. chem. Soc. A, In press.

^{3.} J. Goubeau and H. Behr, Z. anorg. allg. Chem. 272, 2 (1953).

^{4.} K. Moedritzer and J. R. Van Wazer, Inorg. Chem. 3, 268 (1964).

^{5.} H. G. Heal, Nature, Lond. 158, 672 (1946).

presence of an aluminium triiodide catalyst, the vapour and liquid phase reactions with hydrogen iodide yielded silicon tetrafluoride, methyl iodide, perfluorodisiloxane, but no trifluorosilyl iodide.

The reaction with boron tribromide on the other hand proved to be a convenient synthesis of trifluorosilyl bromide; the other (less volatile) product was very unstable, but we were able to obtain a vapour phase i.r. spectrum which indicated the presence of CH_3O- and B-Br groups, and a molecular weight consistent with the formula MeOBBr₂. The behaviour of this product was consistent with the reported decomposition of MeOBBr₂ into methyl bromide, boron tribromide, and a solid formulated as $B_3O_4Br[6]$.

The analogous reactions with boron trifluoride and trichloride proceeded almost quantitatively according to the equation:

$$MeOSiF_3 + BX_3 \rightarrow MeOBX_2 + XSiF_3$$
 (X = F, Cl).

Methoxyboron difluoride and dichloride were found to be appreciably more stable than the dibromide.

EXPERIMENTAL

All manipulations (except the preparation of MeOSiCl₃ and the investigation of the solid decomposition products of MeOBBr₂) were carried out in a conventional pyrex vacuum system with rigorous exclusion of air and moisture. Known volatile compounds were identified spectroscopically and by their distillation properties in the vacuum system. Vapour-phase i.r. spectra were recorded using a Perkin-Elmer 457 spectrometer; ¹⁹F NMR spectra were recorded at 56-458 MHz using a Perkin-Elmer R 10 spectrometer, and ¹H NMR spectra at 100 MHz on a Varian Associates HA 100 instrument. Fluorine chemical shifts are expressed in ppm from the Cl₃CF solvent resonance. Mass spectra were recorded using an A.E.I. MS9 spectrometer.

Reactions

SiCl₄ and MeOH. 280 m-mole of dry methanol was allowed to drip into an ice-cooled stirred solution of 250 m-mole SiCl₄ in 75 ml dry Et₂O under reflux, the top of the condenser being fitted with a drying tube. When all the MeOH had been added, the mixture was refluxed for 1 hr to remove HCl. The fraction distilling between 75° and 80° was transferred to the vacuum line and distilled *in vacuo*. The NMR spectrum of a solution in cyclohexane showed signals at $\tau = 6.30$ (J($^{13}C - H$) = 145 Hz), 6.38 and 6.45, in order of decreasing intensity. These were assigned to Cl₃SiOMe, Cl₂Si(OMe)₂ and ClSi(OMe)₃ respectively [4]; it is probable that slow disproportionation was taking place in the NMR tube at room temperature. The crude Cl₃SiOMe was used without further purification.

Cl₃SiOMe and SbF₃. Crude Cl₃SiOMe was distilled through a column of powdered SbF₃ which had been dried in an oven at 65° for several hr before use. A hot band passed along the column as the reaction proceeded, and the column partially disintegrated owing to the formation of slightly volatile antimony chlorides. Fractionation yielded F₃SiOMe and SiF₄ as the main volatile products, the crude F₃SiOMe thus obtained being used in the large scale preparation of F₃SiBr without further purification. A sample was further purified by distillation through -96° and condensation at -120° , and the middle fraction of this sample used for the determination of the physical and spectroscopic properties of F₃SiOMe. The molecular weight was found to be 116 in the vapour phase (calc. 116·1); the sample was tensimetrically pure at -79° and had a vapour pressure of 15 mm at this temperature; at -49° , the vapour pressure rose slowly, indicating disproportionation in the liquid phase. I.R. ν_{max} : 3052 m, 3000 sh, 2976 s, 2964 s, 2880 s, 2872 s, 2868 s, 2832 sh, 2146 vw, 2102 vw, 2070 vw, 1940 vw, 1900 w, 1860 w, 1714 vw, 1553 w, 1516 w, 1483 sh, 1477 sh, 1470 m, 1465 sh, 1458 sh, 1404 vw, 1316 sh, 1271 sh, 1260 sh, 1214 vs, 1205 vs, 1198 sh, 1180 sh, 1171 vs, 1164 vs, 1144 vs, 1138 vs, 1132 vs, 997 vs, 993 vs, 936 vs, 928 vs, 924 sh, 892 m, 772 b, 742 sh, 736 m, 669 b, 412 sh, 384 vs, 375 vs; (vs = very strong, s = strong,

6. J. Goubeau, H. J. Becher and F. Griffel, Z. anorg. allg. Chem. 282, 86 (1955).

m = medium, w = weak, vw = very weak, sh = shoulder, b = broad). ¹H NMR (in Cl₃CF/TMS solvent mixture): strong single line, $\tau = 6.24$, with ¹³C satellites, J(¹³CH) = 147 Hz; weak single line at $\tau = 6.33$. ¹⁹F NMR (of same sample): strong single line, $\phi = 162.1$ ppm with ²⁹Si satellites, J(²⁹SiF) = 181 Hz (MeOSiF₃); weak signals at $\phi = 164.8$ (SiF₄) and 160.1 ppm (F₂Si(OMe)₂?). Attempts to further resolve the main ¹H and ¹⁹F peaks were not successful. The base peak of the mass spectrum was assigned to SiF₃⁺, very strong peaks were also found due to CHO⁺, CH₃O⁺ and F₃SiOCH₂⁺. The fragments SiF₃²⁺, SiF₄⁺, SiF₂⁺, SiF₃, SiF₄⁺, SiF₃OCH⁺, SiF₃OC+, SiF₂OCH₃⁺, and SiF₂(OCH₃)₂⁺ were also found, but no significant parent ion was detected. Some hydrolysis products, e.g. Si₂OF₅⁺ and Si₂OF₄(OCH₃)⁺, were also identified.

 F_3SiOMe and SbF_3 with $SbCl_5$ catalyst. This reaction yielded SiF_4 quantitatively, and was used to estimate the silicon in the F_3SiOMe . Found: Si, 23.8%; calc. Si, 24.2%.

Cl₃SiOMe and KHF₂. Crude SiCl₃OMe was distilled through a column of dry powdered KHF₂. The product consisted mainly of unchanged starting material, together with some HCl and SiF₄. No SiF₃OMe was detected.

F₃SiOMe and BBr₃. 0.83 m-mole F₃SiOMe and 0.89 m-mole BBr₃ were condensed into a cold finger attached to a 1 l. bulb and allowed to warm to room temperature. After 12 hr the volatile products were fractionated; some involatile white solid remained in the cold finger. The fraction involatile at -78° deposited a white solid when distilled from trap to trap, had a molecular weight of 204 (calc. for MeOBBr₂, 201; for BBr₃, 251), and gave a gas phase i.r. spectrum indicating the presence of MeOand B – Br groups, but not of MeBr. The NMR spectrum of a solution in cyclohexane showed singlets at $\tau = 6.09$ (MeOBBr₂?) and 7.36 (MeBr). This behaviour is consistent with the known decomposition of MeOBBr₂ into MeBr and a solid formulated as B₃O₄Br[6]. Fractionation of the more volatile components yielded 0.15 m-mole SiF₄, 0.65 m-mole SiF₃Br ($\phi = 125.8$ ppm[7]). 0.35 m-mole MeBr and a trace of (SiF₃)₂O.

The reaction was carried out on a larger scale with a 50 per cent excess of BBr₃, 8.9 m-mole F₃SiOMe giving 7.5 m-mole SiF₃Br on fractionation. The white involatile solid which had formed on the wall of the bulb was scraped off in a dry box; the i.r. spectrum indicated the presence of MeO-groups, and bromine analysis (by hydrolysis followed by Volhard titration) gave 35-40% Br for various samples.

F₃SiOMe and BCl₃. 0.61 m-mole F₃SiOMe and 0.72 m-mole BCl₃ were condensed into a cold finger attached to a 1 l. bulb and allowed to warm to room temperature, leaving a white solid in the finger. After 12 hr this solid had volatilised. Fractionation of the products gave 0.6 m-mole MeOBCl₂ (identified by vapour phase i.r. spectrum [8] and molecular weight: Found, 112; calc. 112), 0.05 m-mole BCl₃ and 0.6 m-mole of a mixture of silicon chlorofluorides, identified by NMR as consisting mainly of SiF₃Cl ($\phi = 135.9$ ppm) with small quantities of SiF₄ and SiF₂Cl₂[7].

F₃SiOMe and BF₃. 0.99 m-mole F₃SiOMe and 0.99 m-mole BF₃ were condensed into the cold finger attached to a 1 l. bulb, and allowed to warm to room temperature; a colourless liquid remained in the finger. The mixture was allowed to stand at room temperature for 20 hr. Fractionation yielded 0.99 m-mole of SiF₄ containing a trace of (SiF₃)₂O, and a less volatile fraction which deposited traces of involatile solids when distilled from trap to trap, and had a vapour pressure of about 7 mm at 22°. The vapour phase i.r. spectrum, ¹⁹F NMR spectrum (broad single line at $\phi = 154.4$ ppm) and 'H NMR spectrum (singlet at $\tau = 6.15$ with satellites having J(¹³CH) = 152 Hz) were consistent with the formula MeOBF₂. A shoulder at $\tau = 6.10$ and a few very weak peaks in both NMR spectra may have been due to small quantities of disproportionation or decomposition products.

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