Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

A DIRECT PREPARATION OF SOME PENTAFLUOROPHENYL-CONTAINING SILANES

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(Received January 9th, 1968)

SUMMARY

The reaction of pentafluorobromobenzene with both tetraethoxysilane and tetrachlorosilane, by a modified Grignard method, leads to the formation of compounds of the type $(C_6F_5)_nSiX_{4-n}$ where $X=OC_2H_5$ and Cl and $n=1$–4.

These compounds have been characterized by physical methods, elemental analysis, interconversion and the preparation of derivatives.

INTRODUCTION

Normally, using a Grignard or lithium synthesis, it is possible to substitute halo- and alkoxy-silanes with organic groups (R). Usually a mixture of variously substituted silanes is obtained and it appears that the Grignard synthesis of organohalosilanes can be treated as a series of successive reactions of the type $AX_4+RY \rightarrow AX_mR_n+nXY$[1]. The lithium synthesis is considered to be very similar to that of the Grignard reaction, though the higher reactivity of the organolithium reagent, which is one of its main advantages, leads to more highly substituted silanes.

However the reaction of pentafluorophenylmagnesium bromide[2,3] or pentafluorophenyllithium[3] with tetrachlorosilane has been shown to yield only the fully substituted tetrakis(pentafluorophenyl)silane in low yield. Irrespective of the mode of addition or the relative amounts of reagents used, the partially substituted products $(C_6F_5)_nSiCl_{4-n}$ could not be obtained directly from these reactions. Recently it has been reported[4] that methyl(pentafluorophenyl)diethoxysilane and bis(pentafluorophenyl)diethoxysilane have been synthesized by the Grignard method though no details of the experimental procedure were given.

We would like to report here a direct synthesis of compounds of the type $(C_6F_5)_nSiX_{4-n}$ where $X=OC_2H_5$ and Cl and $n=1$–4 using a Grignard synthesis.

RESULTS AND DISCUSSION

Tamborski and co-workers[5] explained the formation of the tetrakis(pentafluorophenyl)silane on the basis that once one pentafluorophenyl-group is introduced the reactivity of the remaining chlorine atoms attached to silicon is enhanced and further replacement is rapid to give the fully substituted silane. A further complication which accounts for the low yield, appears to be that tetrachlorosilane catalyses the decomposition of the Grignard or lithium reagent (prepared from pentafluorobromobenzene) to give polymeric sideproducts.

It has been shown[6] that tetraethoxysilane is less reactive than tetrachlorosilane towards Grignard reagents and that the resulting substituted ethoxysilanes have similar properties to the more reactive substituted chlorosilanes. It was thought that the Grignard reagent with tetraethoxysilane might yield the desired partially substituted silanes. The Grignard reagent was preferred to the more reactive lithium reagent which, we considered, would lead preferentially to the formation of the tetrasubstituted silane.

The reaction of pentafluorophenylmagnesium bromide and tetraethoxysilane was examined in detail. The normal procedure of adding the preformed Grignard reagent, in a suitable solvent, to tetraethoxysilane gave, as the only product isolated. the known tetrakis(pentafluorophenyl)silane in low yield. It was thought that this problem of tetrasubstitution and the formation of side products might be due to high local concentrations of Grignard reagent which, even with high speed stirring, must occur at the point of addition. To overcome these high concentrations we proposed to modify the Grignard synthesis and attempt to form the Grignard reagent *in situ* using tetraethoxysilane as both solvent and reactant. No reaction could be induced between pentafluorobromobenzene, tetraethoxysilane and magnesium turnings when mixed together. Even the addition of ethylbromide failed to promote any discernible reaction. However upon adding diethyl ether dropwise a "critical concentration" was reached and a vigorous reaction observed. Examination of this reaction mixture by gas chromatography showed, apart from starting materials, two major components, (pentafluorophenyl)triethoxysilane and bis(pentafluorophenyl)diethoxysilane, and two trace components thought to be the tri- and tetra-substituted silanes.

These ethoxysilanes were characterized by molecular weight determination (mass spectrometry and vapour pressure osmometry) and elemental analysis. The infrared spectra showed the characteristic bands associated with pentafluorophenyl-[7,3] and ethoxy-[8] groups. The NMR spectra were also consistent with the proposed structures.

Further evidence for these structures was obtained as follows: Examination of the reaction of methylmagnesium iodide and (pentafluorophenyl)triethoxysilane showed that, using excess of the Grignard reagent, the fully substituted silane, trimethyl(pentafluorophenyl)silane was formed in more than 90% yield. This was identical to the product from trimethylchlorosilane and pentafluorophenylmagnesium bromide in diethyl ether[9]. Using equimolar ratios of methylmagnesium iodide and the triethoxysilane afforded methyl(pentafluorophenyl)diethoxysilane and dimethyl(pentafluorophenyl)ethoxysilane in the ratio 2:1 with a trace of trimethyl(pentafluorophenyl)silane. These structures were confirmed by proton NMR spectroscopy. With bis(pentafluorophenyl)diethoxysilane, methylmagnesium iodide gave dimethylbis(pentafluorophenyl)silane in high yield. Both the ethoxysilanes were smoothly converted into the chlorosilanes by acetyl chloride though reaction of aqueous ethanolic HF resulted, not in the formation of the fluorosilanes. but in complete and rapid cleavage of the pentafluorophenyl groups.

This modified Grignard synthesis was then applied to tetrachlorosilane. Diethyl ether was added dropwise to a mixture of pentafluorobromobenzene, tetrachlorosilane and magnesium turnings until a reaction was observed. Examination of the reaction mixture by analytical gas chromatography showed, apart from starting materials and several minor components, four major components which corresponded to the four possible (pentafluorophenyl)chlorosilanes. It is interesting to note that in the reaction with tetraethoxysilane, very little of the tri- and tetra- substituted silanes were formed whereas, under identical conditions with tetrachlorosilane, an appreciable amount of the tetrasubstituted compound was formed together with side products formed by the decomposition of the Grignard reagent. This would appear to confirm the view[5] that the introduction of pentafluorophenyl groups activate the remaining chlorine atoms so that further replacement is rapid. Therefore, only by keeping the concentration of the Grignard reagent low can the partially substituted silanes be prepared directly.

The (pentafluorophenyl)chlorosilanes were separated by fractional distillation under reduced pressure though prolonged refluxing appeared to lead to substantial decomposition. These chlorosilanes were characterized by estimation of chlorine, conversion to the ethoxysilanes using dry ethanol/pyridine and comparison of IR spectra and retention times on the gas chromatograph with the previously prepared characterized compounds.

EXPERIMENTAL

Diethyl ether and all hydrocarbon solvents used were dried over sodium. Tetrahydrofuran (THF) was distilled from lithium aluminium hydride immediately before use. Ethanol was dried by distillation from magnesium turnings[10]. Chromatographic analyses were carried out on a Pye (model 104) gas chromatograph using a 6′ column (packing 20% SIL M.S. 2430) with helium as carrier gas. Specific operating temperatures are mentioned in the text. Pentafluorobromobenzene (supplied by the Imperial Smelting Corporation Limited), tetraethoxysilane and tetrachlorosilane were used as supplied without further purification. Molecular weights were determined by either vapour pressure osmometry (Mechrolab V.P. Osmometer) or mass spectrometry. All boiling points and melting points are uncorrected.

(*a*). *The reaction of pentafluorobromobenzene and tetraethoxysilane*

Pentafluorobromobenzene (24.7 g, 0.1 mole), magnesium turnings (2.65 g, 0.11 g-atom) and tetraethoxysilane (83.2 g, 0.4 mole) were mixed at room temperature and diethyl ether added dropwise to the vigorously stirred mixture until a critical concentration was reached (approx. 60 ml). A vigorous reaction was observed and cooling (ice bath) was necessary to maintain a gentle reflux. Stirring and refluxing was continued for a further 18 h to complete the reaction (Colour test I[11] negative). The mixture was then cooled to room temperature, excess n-heptane added to precipitate the magnesium salts and filtered under an atmosphere of dry nitrogen until a clear pale yellow solution was obtained. Solvents and unchanged tetraethoxysilane were removed and the residue fractionally distilled to give (pentafluorophenyl)triethoxysilane (compound I), 17.2 g (55%), b.p. 235–238° (Found: C, 43.2; H, 4.1; Si, 8.51; mol. wt., 324. $C_{12}H_{15}F_5O_3Si$ calcd.: C, 43.6; H, 4.55; Si, 8.48%; mol. wt., 330.), and bis(pentafluorophenyl)diethoxysilane (compound II), 12.5 g (35%), b.p. 298–303° (Found: C, 42.1; H, 2.34; Si, 6.3; mol. wt., 452. $C_{16}H_{10}F_{10}O_2Si$ calcd.: C, 42.5; H, 2.22; Si, 6.2%; mol. wt., 452.), with a trace of a white solid thought to be tris(pentafluorophenyl)ethoxysilane. Compounds (I) and (II) were further purified by gas chromatography.

(b). The reaction of compound (I) and methylmagnesium iodide (molar ratio 1 : 6)

Methylmagnesium iodide was prepared in the normal way from methyl iodide (4.26 g, 0.03 mole) in diethyl ether (6.0 ml). Compound (I) (1.65 g 0.005 mole) in diethyl ether (1.5 ml) was then added dropwise to the cooled methylmagnesium iodide solution and the whole refluxed and stirred for 2 h. The reaction mixture was cooled, hydrolysed with 4 *N* H_2SO_4 and extracted with ether. The ether extract was dried ($MgSO_4$) and distilled to give trimethyl(pentafluorophenyl)silane (1.1 g), b.p. 170° (759 mm). This was identical to a sample prepared from the reaction of trimethylchlorosilane and pentafluorophenylmagnesium bromide in diethyl ether[9].

(c). The reaction of compound (I) and methylmagnesium iodide (molar ratio 1 : 1)

Methylmagnesium iodide solution in diethyl ether was prepared from methyl iodide (1.42 g, 0.01 mole). This solution was diluted to 10 ml by the addition of diethyl ether, filtered, and then added dropwise to a mixture of compound (I) (3.30 g 0.01 mole) in diethyl ether (3.0 ml). After 2 h refluxing, the mixture was cooled to room temperature and n-heptane added to precipitate the magnesium salts. Filtration and removal of solvents left a yellow/brown oil (2.5 g).

Examination by gas chromatography (column temperature 140°) showed three major and one trace component. These were separated by gas chromatography and shown, by proton NMR spectroscopy to be (*i*) trimethyl(pentafluorophenyl)silane (trace), (*ii*) dimethyl(pentafluorophenyl)ethoxysilane (0.5 g) (integrated proton ratio found; 5.95 : 5; calcd., 6 : 5), (*iii*) methyl(pentafluorophenyl)diethoxysilane (1.1 g) (integrated proton ratio found, 2.95 : 10; calcd., 3 : 10) and (*iv*) unchanged compound (I) (0.9 g).

(d). The reaction of compound (II) with methylmagnesium iodide

Methylmagnesium iodide was prepared from methyl iodide (4.26 g, 0.03 mole) in diethyl ether. To this Grignard solution was added compound (II) (4.52 g, 0.01 mole) in diethyl ether (6.0 ml). The mixture was refluxed for 2 h and worked up as in (*b*). Distillation gave bis(pentafluorophenyl)dimethylsilane (3.0 g), b.p. 140–144° (14 mm). (Found: Si, 6.9; $C_{12}H_6F_{10}Si$ calcd.: 7.1 %.)

(e). The reaction of compounds (I) and (II) with aqueous ethanolic HF

In both cases the silane was dissolved in the minimum amount of ethanol and a three molar excess of aqueous HF (39–43 % w/w HF) added dropwise. An immediate reaction was observed and a gas evolved. Addition of water precipitated a colourless oil which was shown to be pentafluorobenzene.

(f). The reaction of compounds (I) and (II) with acetyl chloride

Compound (I) (1.65 g, 0.005 mole) was dissolved in excess acetyl chloride (4.0 ml) and left for 48 h at room temperature. Distillation under reduced pressure gave (pentafluorophenyl)trichlorosilane (1.4 g), b.p. 80–84° (14 mm).

In a similar manner compound (II) gave bis(pentafluorophenyl)dichlorosilane in good yield, b.p. 180–185° (16 mm).

(g). The reaction of pentafluorobromobenzene and tetrachlorosilane

Pentafluorobromobenzene (24.7 g, 0.1 mole), magnesium turnings (2.67 g, 0.11 g-atom) and tetrachlorosilane (68 g, 0.4 mole) were mixed at room temperature under an atmosphere of dry nitrogen and diethyl ether added dropwise to the stirred mixture. After the addition of 50 ml of diethyl ether a reaction was observed and cooling was necessary to moderate this reaction. The resulting mixture was stirred for a further 12 h at room temperature (colour test I negative), the magnesium salts precipitated by the addition of n-heptane and the filtered solution distilled

After removal of starting materials and solvents a white solid, tetrakis(pentafluorophenyl)silane was precipitated (4.0 g), m.p. 248–250°. (Found: C, 41.0; H, < 0.1; Si, 3.91; mol.wt., 696. $C_{24}F_{20}Si$ calcd.: C, 41.4; H, 0.0; Si, 4.0%; mol.wt., 696.) Examination of the liquid residue (12.2 g) by gas chromatography (column temperature 170°) showed two major components which were separated by fractional distillation under reduced pressure as (pentafluorophenyl)trichlorosilane (compound III) (2.5 g), b.p. 78–81 (14 mm), and bis(pentafluorophenyl)dichlorosilane (compound IV) (4.8 g), b.p. 82–84 (0.3 mm). Compounds (III) and (IV) were identified by comparison to samples prepared in (*f*) and by estimation of the chloride content by titration with standard alkali.

(h). The reaction of compounds (III) and (IV) with ethanol

Compound (III) (1.5 g, 0.005 mole) in ether (2.0 ml) was added dropwise to a mixture of dry ethanol (2.0 ml) and pyridine (2.0 ml) at room temperature. Upon standing a white crystalline precipitate of pyridine hydrochloride separated out. The filtered solution was distilled to give (pentafluorophenyl)triethoxysilane (1.0 g) identified by its infrared spectrum and retention time on the gas chromatograph (column temperature 212°).

In a similar manner Compound (IV) was converted to bis(pentafluorophenyl)-diethoxysilane in good yield.

ACKNOWLEDGEMENTS

The Imperial Smelting Corporation Limited for the generous gift of pentafluorobromobenzene, and Dr. A. HOLT for helpful suggestions.

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