[CONTRIBUTION FROM THE RAHWAY RESEARCH LABORATORY OF THE METAL AND THERMIT CORP.]

Preparation of Some Arylchlorosilanes with Arylmagnesium Chlorides[1]

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Diphenyldichlorosilane, phenylmethyldichlorosilane, phenylvinyldichlorosilane, phenyltrichlorosilane, *p*-chlorophenyltrichlorosilane, bis-*p*-chlorophenyldichlorosilane, bis-*p*-methoxyphenyldichlorosilane, and bis-*p*-ethylphenyldichlorosilane have been prepared by the reaction of arylmagnesium chlorides with appropriate silicon chlorides.

Since 1904 when the use of a Grignard reagent to prepare organosilicon compounds was reported by Kipping[2] and Dilthey,[3] this method of synthesis of organosilanes has undergone considerable refinement in techniques, and has become a very versatile and popular method for the preparation of these compounds on a laboratory scale. The development of arylmagnesium chloride reagents in this laboratory[4] has afforded the opportunity of preparing arylchlorosilanes utilizing comparatively inexpensive chlorobenzene and some of its derivatives.

As in almost any reaction of a Grignard reagent with silicon tetrachloride to form partially substituted arylchlorosilanes, it was found that a group of successive substitution products was formed.[5] By choosing proper reaction concentrations and temperatures it was possible, in most cases, to produce the desired arylchlorosilanes in good yields. Diphenyldichlorosilane was prepared in a 77% yield by the addition of 2.0 equivalents of phenylmagnesium chloride to 0.9 equivalent of silicon tetrachlororide. Using virtually identical conditions,

$$C_6H_5MgCl + SiCl_4 \xrightarrow[\text{Reflux}]{\text{Heptane}} (C_6H_5)_2SiCl_2$$

it was possible to prepare bis-*p*-chlorophenyldichlorosilane, bis-*p*-methoxyphenyldichlorosilane, and bis-*p*-ethylphenyldichlorosilane from the appropriate arylmagnesium chloride[4] in tetrahydrofuran and silicon tetrachloride in heptane.

The preparation of phenyltrichlorosilane by the addition of 2.0 equivalents of phenylmagnesium chloride to 2.2 equivalents of silicon tetrachloride led to the formation of a fair amount of diphenyldichlorosilane (17%) as well as the desired product (47%). The use of a larger amount of silicon tetrachloride did not seem to change the product balance and, indeed, it complicates the solvent recovery problem because of the proximity of the boiling points of silicon tetrachloride (57.6°) and tetrahydrofuran (65.5°). A similar problem was encountered in the preparation of phenylvinyldichlorosilane.

It was found that greater advantage of the concentration effect could be taken if the tetrahydrofuran were displaced from the stock phenylmagnesium chloride solution by the use of toluene. Toluene was added to the stock solution and most of the tetrahydrofuran removed by distillation. The addition of 2.0 equivalents of phenylmagnesium chloride in toluene to 4.0 equivalents of methyltrichlorosilane in toluene resulted in the preparation of phenylmethyldichlorosilane in a 73% yield, accompanied by a 51% recovery of methyltrichlorosilane.

A hydrocarbon solvent was used in all the reactions to limit the solubility of the magnesium chloride in the reaction solution and to yield a salt from which the solution could be filtered easily. Heptane, when used in the concentrations reported, accomplished both of these tasks very well. The filtered solutions were distilled to virtual dryness leaving only a small amount of salt as residue. In the reactions reported here tetrahydrofuran as received from the du Pont Company, purified virgin tetrahydrofuran and purified recovered tetrahydrofuran were used as solvents in the preparation of the arylmagnesium chlorides. No difference was noted in the behavior of the reactions in comparative duplicate runs provided the solvents were maintained anhydrous. In our hands, tetrahydrofuran exhibited no unusual behavior or hazard provided standard safety precautions were observed.

EXPERIMENTAL

Phenyltrichlorosilane. In a 5.0-l. flask was placed 374.0 g. (2.2 moles) of silicon tetrachloride in 2.0 l. of heptane. Then phenylmagnesium chloride[4] in tetrahydrofuran solution from a 2.0-mole run was added, by means of a dropping funnel, at the rate of 0.5 l. per hr. Excellent stirring and a pot temperature of 40–50° were maintained throughout the addition. After completion of the addition, the mix was refluxed for 2.0 hr. and then allowed to cool to room temperature while the suspended salt settled.

The reaction solution was filtered from the salt *via* a gas dispersion tube[6] to a 5.0-l. flask. Nitrogen pressure of 2–5 lb./in.^{2} was used to force the solution through the dispersion tube. The salt cake was washed with two 250-ml. portions of heptane and the washings were transferred to

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(1) This paper was presented before the 130th Meeting of the AMERICAN CHEMICAL SOCIETY at Atlantic City, N. J., September 1956.

(2) F. S. Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904).

(3) W. Dilthey, *Ber.*, **37**, 319 (1904).

(4) H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn, and R. Cserr, *J. Org. Chem.*, **22**, 1202 (1957).

(5) See E. G. Rochow, *An Introduction to the Chemistry of the Silicones*, John Wiley and Sons, Inc., New York, 1951, p. 35, for a brief discussion of this problem.

(6) Scientific Glass Apparatus Co., Bloomfield, N. J., Catalogue No. G5420.

TABLE I

PREPARATION OF SOME ARYLCHLOROSILANES

Reactants				Analysis, % Cl[a]	
Arylmagnesium Chloride	Silicon Chloride	Products (Yield)	B.P./mm.	Calcd.	Found
C_6H_5MgCl	$SiCl_4$	$C_6H_5SiCl_3$ (47%)	54–57°/0.4	50.4	50.3
		$(C_6H_5)_2SiCl_2$ (17%)	123–126°/2.0	28.0	27.8
C_6H_5MgCl	$SiCl_4$	$(C_6H_5)_2SiCl_2$ (77%)			
		$C_6H_5SiCl_3$ (8%)			
C_6H_5MgCl	CH_3SiCl_3	$CH_3(C_6H_5)SiCl_2$ (73%)	55–58°/1.0	37.0	36.8
		$CH_3(C_6H_5)_2SiCl$ (5%)	112–115°/1.0	15.3	15.1
C_6H_5MgCl	$CH_2{=}CHSiCl_3$	$CH_2{=}CH(C_6H_5)SiCl_2$ (56%)	84–87°/1.5	34.9	34.7
		$CH_2{=}CH(C_6H_5)_2SiCl$ (15%)	133–136°/1.5	14.5	14.3
p-ClC_6H_4MgCl	$SiCl_4$	p-$ClC_6H_4SiCl_3$ (32%)	88–91°/1.5	57.7	57.4
		$(p$-$ClC_6H_4)_2SiCl_2$ (21%)	178–181°/1.5	44.0	44.1
p-ClC_6H_4MgCl	$SiCl_4$	$(p$-$ClC_6H_4)_2SiCl_2$ (39%)			
		p-$ClC_6H_4SiCl_3$ (18%)			
p-$CH_3OC_6H_4MgCl$	$SiCl_4$	$(p$-$CH_3OC_6H_4)_2SiCl_2$ (44%)	194–197°/1.5	22.6	22.8
		p-$CH_3OC_6H_4SiCl_3$ (24%)	94–97°/1.0	44.0	44.2
p-$C_2H_5C_6H_4MgCl$	$SiCl_4$	$(p$-$C_2H_5C_6H_4)_2SiCl_2$ (62%)[b]	163–166°/1.8	22.9	22.7
		p-$C_2H_5C_6H_4SiCl_3$ (13%)	94–97°/1.0	44.4	44.2

[a] % Cl found by hydrolysis and titration with $AgNO_3$ solution. [b] n_D^{20} 1.5694; d_D^{20} 1.1422.

the 5.0-l. flask. The unreacted silicon tetrachloride, tetrahydrofuran, and heptane were removed from the filtrate by distillation at 1.0 atm. The residue was transferred to a 500-ml. flask and distilled under reduced pressure to yield the following fractions.

(1) b. 54–57°/0.4 mm., 198.5 g. (47.0%) of phenyltrichlorosilane.

(2) b. 95–105°/1.0 mm., 10.0 g. (7.0%) of biphenyl.

(3) b. 123–126°/2.0 mm., 42.4 g. (17.0%) of diphenyldichlorosilane.

Phenylvinyldichlorosilane. In a 5.0-l. flask was placed 324.0 g. (2.0 moles) of vinyltrichlorosilane in 2.0 l. of heptane. Then phenylmagnesium chloride in tetrahydrofuran solution from a 2.0-mole run was added at the rate of 0.25 l. per hr. Excellent stirring was maintained. After completion of the addition, the mix was refluxed for 1.0 hr. and then allowed to cool while the salt settled.

The solution was filtered, the salt washed, and the solvents stripped at 1.0 atm. The residue was distilled under reduced pressure to yield 228.2 g. (56%) of phenylvinyldichlorosilane, b. 84–87°/1.5 mm., and 35.9 g. (15%) of diphenylvinylchlorosilane, b. 133–136°/1.5 mm.

Phenylmethyldichlorosilane. In a 5.0-l. flask was placed 598.0 g. (4.0 moles) of methyltrichlorosilane in 2.0 l. of toluene. Then phenylmagnesium chloride in toluene solution[7] from a 2.0-mole run was added at the rate of 0.75 l. per hr. Excellent stirring and a pot temperature of 40° were maintained. After completion of the addition, the mixture was stirred for 2.0 hr. and then the salt was allowed to settle.

The solution was filtered, the salt was washed with toluene, and the unreacted methyltrichlorosilane and toluene were removed at 1.0 atm. The residue was distilled under reduced pressure to yield 277.0 g. (73%) of phenylmethyldichlorosilane, b. 55–58°/1.0 mm., and 12.0 g. (5%) of diphenylmethylchlorosilane, b. 112–115°/1.0 mm.

The solution of methyltrichlorosilane in toluene was carefully fractionally distilled to yield 305.0 g. (51%) of methyltrichlorosilane distilling at 63–70°.

Perchlorophenylmagnesium chloride. In a 2.0-l. flask were placed 142.4 g. (0.5 mole) of hexachlorobenzene 48.7 g. (2.0 g.-atom) of magnesium turnings, 500 ml. of tetrahydrofuran, and one crystal of iodine. The flask was warmed gently and 2.0 ml. of ethyl bromide added. At the first sign of initiation, the heat source was removed and the flask was immersed in a cold water bath. The initiation phase of the reaction is extremely vigorous and it is essential that a water condenser with a large liquid capacity be used. Once the initiation phase was completed, 427.2 g. (1.5 moles) of hexachlorobenzene was added via a solid addition funnel as fast as the reflux rate would allow. When all of the solid had been added, the water bath was removed and the solution was stirred for 1.0 hr. At this time all of the magnesium had been consumed and the perchlorophenylmagnesium chloride was ready for use. The yield, as ascertained by hydrolysis to pentachlorobenzene, was 1.2 moles (60.0%), m.p. 84–86°.

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[7] This technique was outlined in the discussion.