Conversion of Arylsilanes, Arylchlorosilanes, and Siloxanes into Chlorosilanes

By Sheila Mawaziny,* Department of Physical Sciences, The American University in Cairo, 113 Sharia Kasr el Aini, Cairo, U.A.R.

Thirteen chlorosilanes have been prepared by the reaction between phosphorus pentachloride and the corresponding silanes. Yields were between 78-1 and 96-4%. Silicon atoms bearing chlorine or oxygen atoms were less reactive than other silanes. Phenyldichlorosilane failed to react.

PUBLISHED METHODS 1-3 for the conversion of organosilicon hydrides into organosilicon chlorides include the use of chlorine; this method has the disadvantage that chlorination of the organic substituents may occur, or with polysilanes cleavage of the silicon-silicon bond.⁴ Use of organic chlorides has been little used.^{2,3,5}

Attempted partial reduction of phenyltrichlorosilane to give phenyldichloro- and phenylchloro-silane always resulted in the formation of phenylsilane.⁶ Here the preparation of these two compounds by partial chlorination of phenylsilane is described. Nametkin⁷ used phosphorus pentachloride to convert 1,1,1,3,3-pentapropyl- and 1,1,1,3,3-pentabutyl-1,3-disilapropane into 1,1,1,3,3-penta-alkyl-3-chloro-1,3-disilapropanes.

Here the silane and phosphorus pentachloride in carbon tetrachloride was stirred rapidly at room temperature or at the boiling point of the solvent. The reaction was followed by i.r. spectroscopy. For silicon atoms bearing only one hydrogen atom, the disappearance of the characteristic Si-H stretching band at $4 \cdot 4 - 4 \cdot 8 \mu$ indicated completion of the reaction.

For conversion of SiH₂ into SiHCl the reaction was continued until the band at 10.6μ disappeared, while at the same time the silicon hydrogen stretching band developed into a doublet at 4.5 and 4.65μ .

For conversion of SiH₃ to SiH₂Cl the reaction was continued until the band at $10.8 - 11.0 \mu$ disappeared and was replaced by bands at 10.6–10.7 μ and 11.6–11.7 μ . For conversion to SiHCl₂ the reaction was continued until the band at $10.6 - 10.7 \mu$ disappeared.

The results of the chlorinations are given in the Table.

The results show that diphenylsilane is more readily converted into diphenylchlorosilane than the latter is converted to diphenyldichlorosilane; with phenylsilane the first hydrogen atom is readily replaced, the second much less readily replaced, whilst the third is not replaced under these conditions.

Since monochlorination of phenyl-, diphenyl-, and triphenyl-silane takes place with approximately equal ease the presence of a phenyl group has only a slight effect on the ease of chlorination. Replacement of

556. ² B. N. Dolgov, S. N. Borisov, and M. G. Voronkov, Zhur. ¹⁶ (Cham 4bs 1957 51, 16,282.

¹ D. R. Dolgov, S. R. Dorsov, and M. G. Volonkov, *Zmar. Obshchei Khim.*, 1957, 27, 716 (*Chem. Abs.*, 1957, 51, 16,282.
³ F. C. Whitmore, E. W. Pietrusza, and L. H. Sommer, *J. Amer. Chem. Soc.*, 1947, 69, 2108.
⁴ M. Kumada, K. Shina, and M. Yamaguchi, *J. Chem. Soc.*

Japan, Ind. Chem. Sect., 1954, 57, 230.

phenyl groups by methyl groups increases the rate of reaction. Oxygen attached to silicon markedly reduced the rate of reaction (see Table).

37: .1.4

Desetion

		rieia	Reaction
Silane (mol.)	Product	(%)	conditions
Ph _s SiH (1) ª	Ph ₃ SiCl	87.6	Heat 5 hr.
Ph,SiH, (1)	Ph ₂ SiHCl	89.5	R.T.; »
	-		17 hr.
Ph ₂ SiHCl (1) ^a	Ph ₂ SiCl ₂	87.0	Heat 96 hr.
$PhSiH_{3}(1)$	PhSiH ₂ Cl	87.6	R.T.; *
0.11			$27 \mathrm{hr.}$
$PhSiH_3$ (3) ^{a,c}	PhSiHCl ₂	85.3	Heat 12 hr.
$PhSiHCl_2(1)^d$	90% recovery	0	Heat 250 hr.
$H(SiPh_2)_2H(2)^{\alpha}$	Cl(SiPh ₂) ₂ Cl	81.5	Heat 18 hr.
H(SiPh ₂) ₃ H (2) *	$Cl(SiPh_2)_3Cl$	85.0	Heat 3½ hr.
$H(SiPh_2)_4H(2)^a$	$Cl(SiPh_2)_4Cl$	96.4	Heat 2 hr.
$H(SiPh_2)_5H(2)$	Cl(SiPh ₂) ₅ Cl	79.9	Heat 8 hr.
H(SiPhMe) ₂ H (2) ^a	Cl(SiPhMe) ₂ Cl	81.5	R.T.; 🌶
			$45 \min$.
HSiPh ₂ [CH ₂] ₄ SiPh ₂ H	ClSiPh ₂ [CH ₂] ₄ SiPh ₂ Cl	90.1	Heat 6 hr.
(2) a			
$(Me_2SiH)_2O(2)$	(Me ₂ SiCl) ₂ O	78.1	Heat 24 hr.
]]		
ĊH₂•[CH₂]₄•ŚiHPh	CH2•[CH2]4SiClPh	87.2	Heat 2 hr.
(1) a			

^a 10% Excess PCl₅ used. ^b Room temperature. ^c A higher yield was obtained with 3 instead of $\frac{1}{2}$ mol. $\frac{4}{20\%}$ Excess PCl₅. • 5% Excess PCl₅ used.

EXPERIMENTAL

Since the method of preparation of the chlorosilanes varied only in the length of time necessary to complete the reaction and whether or not heating was necessary only one typical preparation is described. All other chlorosilanes had physical constants, e.g. refractive index, b.p., m.p., and density in good agreement with literature values. Silicon and chlorine analyses agreed well with calculated values.

Preparation of Triphenylchlorosilane.-Triphenylsilane (10.42 g., 0.04 moles) in AnalaR carbon tetrachloride (50 ml.) was added rapidly to phosphorus pentachloride (9.16 g., 0.044 moles, 10% excess) in AnalaR carbon tetrachloride (50 ml.) at room temperature. The mixture was heated in refluxing carbon tetrachloride. After 2 hr. the intensity of the Si-H band in the i.r. spectrum was twice as intense as that of the Si-Ph band whilst after 4 hr. it was only one quarter as intense; after a further hour it had disappeared. Volatile components were evaporated off at 15 mm./room temperature and light petroleum (b.p. 60-70°) was added to the residue; the mixture was filtered in a

Chem. Soc., 1954, 76, 4555. ⁷ N. S. Nametkin, A. V. Topchiev, and L. S. Povarov, Doklady Akad. Nauk, S.S.S.R., 1955, 103, 435 (Chem. Abs., 1956, 50, 5515c).

¹ J. W. Jenkins and H. W. Post, J. Org. Chem., 1950, 15,

⁵ C. Eaborn and J. E. Baines, unpublished work, quoted in C. Eaborn, 'Organosilicon compounds,' Butterworths, London,

^{1961,} p. 212. ⁶ M. C. Harvey, W. H. Nebergall, and J. S. Peake, J. Amer.

dry atmosphere to leave a white residue, m.p. $93-97^{\circ}$. Evaporation of the light petroleum gave further solid. The combined residues were recrystallized to give triphenylchlorosilane (10·34 g., 87·6%), m.p. and mixed m.p. $95-97^{\circ}$ (lit. m.p. $95-95\cdot5^{\circ}$); the i.r. spectrum was identical with that of an authentic specimen.

Physical Constants and Analyses of New Compounds. 1,5-Dichlorodecaphenylpentasilane, a white solid, m.p. and mixed m.p. 173—175° (Found: Cl, 7·3, 7·4; Si, 14·2, 14·1. $C_{60}H_{50}Cl_2Si_5$ requires Cl, 7·24; Si, 14·27%), i.r. spectrum superimposable on that of an authentic specimen. 1,6-Dichloro-1,1,6,6-tetraphenyl-1,6-disilahexane, a white solid, m.p. 114—116° (Found: Si, 11·1, 11·3; Cl, 14·2, 14·5. $C_{28}H_{28}Cl_2Si_2$ requires Si, 11·4; Cl, 14·46%).

1-Chloro-1-phenyl-1-silacyclohexane, a colourless liquid, b.p. $87-89^{\circ}$, n_p^{24} 1.536 (Found: Si, 13.17, 13.20. $C_{11}H_{35}$ ClSi requires Si, 13.33%). For further proof of identification this compound was converted into the known compound 1,1-diphenyl-1-silacyclohexane, which was identified by its physical constants.

[9/1605 Received, September 18th, 1969]