

(HALOPHENOXY)SILANES. VIII*

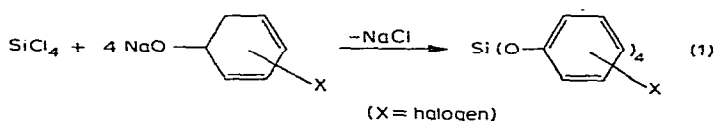
ROSHDY M. ISMAIL AND HANS J. KOETZSCH

Zentrallabor, Dynamit Nobel A.G., Troisdorf (Germany)

(Received March 1st, 1967)

In contrast to other phenols¹ polyhalophenols, especially those containing *ortho*-substituents, condense slowly and incompletely with functional silanes.

Attempts have already been made to prepare halogenated phenoxysilanes. One such procedure is the reaction of the corresponding sodium phenoxides with halosilanes (eqn. 1) in xylene². Tetraphenoxysilanes, derived from pentachlorophenol and 2,4,6-trichlorophenol, were prepared in this way for the first time in yields of about 30%. Diorganodichlorosilanes³ gave products in about 60% yield by this method.



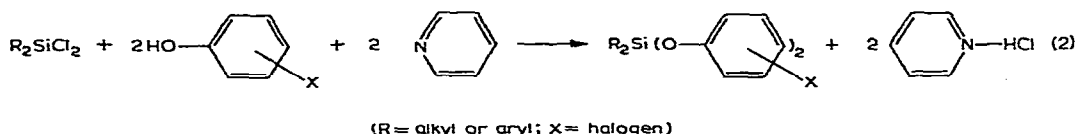
The unavoidable use of metallic sodium or reactive alkali-metal compounds in the preparation of the sodium phenoxides leads to large amounts of by-products in addition to inorganic salts. The latter considerably complicate the separation of the pure halogenated phenoxysilanes since these compounds are rather insoluble and are easily hydrolysed by moisture.

Other methods for preparing phenoxysilanes include the transesterification of readily accessible esters^{4,5} e.g. ethoxysilanes, in the presence of alkaline or acid catalysts such as *p*-toluenesulphonic acid^{2,7}, and the direct condensation of halosilanes with phenols in the presence, or absence, of solvent, with the evolution of hydrogen chloride. The condensation reaction between pentachlorophenol and ethoxysilanes or chlorosilanes proceeds very slowly and incompletely and reaction ceases before the desired halogenated phenoxysilanes have formed to any extent.

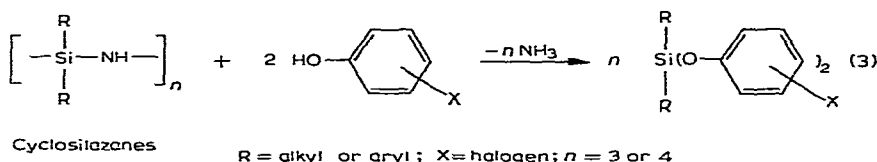
A more suitable method synthesising diorganobis(polyhalophenoxy)silanes is the condensation of the corresponding diorganodichlorosilanes with polyhalophenols in the presence of stoichiometric amounts of pyridine⁷ (eqn. 2). However, tetrachlorosilane and pentachlorophenol, in the presence of pyridine give only the undesired pyridinium salt of pentachlorophenol. In contrast, alkenylchlorosilanes react more readily than the saturated organochlorosilanes.

Organo-substituted silazanes react easily with polyhalophenols with evolution of ammonia or amines to give the corresponding organo- or organoxy(halo-

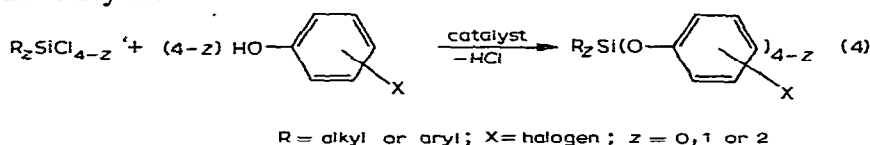
* For Part VII see R. M. ISMAIL, *Fette, Seifen, Anstrichmittel*, 69 (1967) 172.



phenoxy)silanes in a pure state and in high yield (eqn. 3). Small amounts of alkali in the form of sodium hydride, amide, or phenoxide^{6,8,9} markedly catalyse the reaction. This contrasts with the fact that silazanes are relatively alkali stable.



This paper describes a simple method (*cf.* refs. 11 and 12) for the preparation of (polyhalophenoxy)silanes from chlorosilanes and polyhalophenols in the presence of amine catalysts:



As mentioned previously, the reaction between pentachlorophenol and tetrachlorosilane proceeds very slowly in the absence of catalysts. Only a small quantity of hydrogen chloride is evolved and the esterification is essentially incomplete. Upon the addition of N,N-dimethylaniline, a violent evolution of hydrogen chloride sets

TABLE 1

HALOGENATED TETRAPHENOXYSIANES FROM TETRACHLOROSILANE

Starting phenol	M.p. (b.p.)	Yield	Analysis: calcd./found		
			C	X	Si
Pentafluorophenol	80°	93%	37.89	49.94	3.69
	167°/1.0 mm		37.94	50.10	3.71
2,4,5-Trichlorophenol	200°	74%	35.42	52.32	3.45
			35.27	51.89	3.71
2,3,4,6-Tetrachlorophenol	225°	87%	30.22	59.68	2.96
	(benzene)		29.91	59.42	3.22
Pentachlorophenol	285-6°	97%	26.45	65.18	2.57
	(toluene)		26.61	65.07	2.61
2,4,6-Tribromophenol	225°	84%	20.97	69.74	2.04
	(CCl ₄)		21.11	69.60	2.31
Pentabromophenol	365-6°	96%	14.58	80.86	1.42
			14.88	80.95	1.68

TABLE 2

ORGANO(HALOPHENOXY)SILANES OF THE GENERAL FORMULA RSi(OR')_3

R	R'	M.p.	Yield	Analysis: calcd./found				
				C	H	X	Si	
H	Pentafluorophenyl	54° ^a	78 %	37.40	0.17 ^b	48.44	4.76	
				37.31	0.15 ^b	48.11	4.89	
H	Pentachlorophenyl	152° dec. (CCl ₄)	89 %	26.18	0.12 ^b	64.47	3.40	
				25.96	0.11 ^b	64.40	3.68	
H	2,4,6-Tribromophenyl	159° dec. (CCl ₄)	81 %	21.26	0.08 ^b	70.68	2.76	
				21.51	0.06 ^b	71.01	2.92	
H	Pentabromophenyl	170° dec. (toluene)	88 %	14.50		80.36	1.88	
				14.74		79.98	2.02	
Methyl	Pentachlorophenyl	224–6° (cyclohexane)	81 %	27.19		63.28	3.34	
				27.27		63.02	3.50	
Ethyl	Pentachlorophenyl	206° (cyclohexane)	79 %	28.18		62.30	3.28	
				28.22		62.17	3.51	
Vinyl	Pentachlorophenyl	200° (cyclohexane)	78 %	28.24		62.42	3.29	
				28.19		62.35	3.36	
Vinyl	2,4,6-Tribromophenyl	139–40° (toluene)	92 %	23.00		68.81	2.68	
				22.76		68.56	2.79	
Propyl	Pentachlorophenyl	157° (hexane)	64 %	29.10		61.31	3.23	
				29.02		61.07	3.31	
Decyl	Pentachlorophenyl	104–5° (pentane)	69 %	34.83	2.19	55.05	2.90	
				35.00	2.55	54.88	3.02	
Cyclohexyl	Pentachlorophenyl	225–7° (cyclohexane)	62 %	31.76	1.23	58.63	3.08	
				32.02	1.61	58.41	3.11	
Phenyl	Pentachlorophenyl	193–5° (benzene)	72 %	32.00		58.97	3.11	
				32.00		58.79	3.14	
		benzene solvate dec. 80–90°		36.78	1.13	54.24	2.86	
				36.74	1.50	54.21	2.91	

^a B.p. 117–119°/1.0 mm. ^b Active hydrogen.

in and the esterification is complete within a few hours. The required product crystallising from the reaction medium is virtually pure. Many amines, such as N,N-dimethylaniline, *p*-bromo-N,N-dimethylaniline and N,N,N',N'-tetramethylbenzidine are suitable catalysts and the concentration usually employed is 0.1 mol of catalyst to 2 mol % of halosilane.

Other polyhalophenols such as 2,4,6-tribromophenol, pentabromophenol, pentafluorophenol and the di-, tri- and tetrachlorophenols can be esterified in good yield by this simple method (Table 1). Suitable starting chlorosilanes such as the commercially available diorganodichlorosilanes and organotrichlorosilanes can also be esterified in the same way (Tables 2, 3 and 4).

The reaction is carried out at elevated temperatures with reactants in the molten state or dissolved in inert solvents such as ethers, benzene or toluene etc.

TABLE 3

ORGANO(HALOPHENOXY)SILANES OF THE GENERAL FORMULA $R^1R^2Si(OR')_2$

R^1	R^2	R'	$M.p., b.p., n_D^{20}$	Yield	Analysis: calcd./found			
					C	H	Cl(Br, F)	Si
H	Methyl	Pentachlorophenyl	140–42° (hexane)	90%	27.16 27.11	0.17 ^a 0.2 ^a	61.70 61.45	4.87 4.92
Methyl	Methyl	Pentachlorophenyl	153° (toluene)	90%	28.54 28.67	1.03 1.44	60.20 59.88	4.76 4.95
		Pentabromophenyl	175° (toluene)	80%	16.27 16.00	0.59 0.92	77.26 76.89	2.71 3.02
Methyl	Vinyl	2,4,5-Trichlorophenyl	200–3°/0.3 mm n_D^{20} 1.5829	90%	38.91 38.64	2.18 2.40	46.00 45.82	6.04 6.21
		2,4,6-Trichlorophenyl	205–9°/0.9 mm n_D^{20} 1.5762	90%	38.91 38.72	2.18 2.50	46.00 45.76	6.04 6.19
		2,3,4,6-Tetrachlorophenyl	228–31°/1.0 mm m.p. 76–7°	78%	33.88 33.89	1.52 1.70	53.28 53.00	5.26 5.38
		Pentachlorophenyl	128°	90%	30.00 30.21	1.01 1.38	59.02 58.77	4.66 4.81
		2,4,6-Tribromophenyl	110–1°	76%	24.71 24.57	1.38 1.66	65.78 65.29	3.46 3.70
Phenyl	Phenyl	Pentachlorophenyl	205°	80%	40.43 40.09	1.41 1.70	49.72 49.62	3.93 4.04

^a Active hydrogen.

TABLE 4

DIFFERENT HIGHER ORGANO(HALOPHENOXY)SILANES

Product	$M.p.$	Yield	Analysis: calcd./found			
			C	H	Cl(Br)	Si
1,1,1,4,4,4-Hexakis(pentachlorophenoxy)-1,4-disilabutane	338° (chlorobenzene)	94%	27.16 27.39		63.44 63.18	3.42 3.63
1,1,1,4,4,4-Hexakis(2,4,6-tribromophenoxy)-1,4-disilabutane	257–8° (benzene)	74%	22.06 22.40	0.78 1.02	69.58 69.10	2.72 3.01
1,1,1,4,4-Pentakis(pentachlorophenoxy)-1,4-disilapentane	238° (benzene)	82%	27.42 26.94	0.5 0.7	62.00 61.67	3.96 4.00

The halosilane and phenol are preferably used in a stoichiometric ratio, *i.e.* 1 mole of halogenated phenol per mole of chlorine in halosilane. However, the yields of (halophenoxy)silanes can be improved by using an excess of the phenol. The condensation takes place promptly with evolution of the stoichiometric quantity of gaseous hydrogen chloride and the halogenated phenoxysilanes are obtained in good yields and in a degree of high purity.

Some of the orthosilicates and most of the organosilane esters did not crystallise spontaneously from the reaction mixture. In these cases the solutions were

concentrated and the silane esters crystallised or precipitated by adding other suitable dry solvents, such as low aliphatic hydrocarbons. Phenyltris(pentachlorophenoxy)-silane crystallized from benzene as a 1 : 1 complex which evolved benzene quantitatively on heating (80–90°) to give the pure phenoxysilane, m.p. 193–195°.

The (halophenoxy)silanes must be recrystallized with complete exclusion of moisture, since these compounds are sensitive to water, especially in solution and at elevated temperatures. They can, however, be stored in crystalline form for long periods at room temperature without decomposition.

EXPERIMENTAL

Tetrakis(pentachlorophenoxy)silane

Pentachlorophenol (1065 g) (m.p. 188–190°, from hexane) was suspended in dry toluene (2.5 l) and 1 ml N,N-dimethylaniline was added. After heating to 56°, tetrachlorosilane (170 g) was added dropwise with stirring during 2–3 h. The reflux condenser was cooled to –10° during the addition to prevent entrainment of tetrachlorosilane with the hydrogen chloride evolved. After the evolution of 30–40% of the theoretical amount of hydrogen chloride the reaction was completed by refluxing the mixture for 12 h. The product which precipitated near the end of the reaction in 97% yield had m.p. 277–9°. It may be recrystallised from toluene, chlorobenzene, or tetrachloromethane with exclusion of moisture. The pure product melts at 285–6°.

n-Decyltris(pentachlorophenoxy)silane

Pentachlorophenol 79.95 g (0.30 mole) was dissolved in 350 ml of toluene at 120° in a three-necked flask equipped with a condenser, an agitator and nitrogen inlet and 27.5 g (0.10 mole) of n-decyltrichlorosilane and 0.4 ml of N,N-dimethylaniline were added to the solution. A strong evolution of hydrogen chloride immediately set in. The hydrogen chloride gas was flushed out of the reaction mixture with nitrogen and reaction was complete after about 12–24 h. The toluene was then distilled off and the product was recrystallised from toluene or acetic ester. The yield of n-decyltris(pentachlorophenoxy)silane was over 90%, m.p. 104–5°.

SUMMARY

A new simple process for the preparation of silane esters of halogenated phenols is described. The reaction of halogenated phenols and chlorosilanes is catalysed by certain types of amines to produce nearly quantitative yields of halogenated phenoxysilanes.

REFERENCES

- 1 R. SCHWARZ AND W. KUCHEN, *Chem. Ber.*, 86 (1953) 1144.
- 2 P. D. GEORGE AND A. E. NEWKIRK, *J. Org. Chem.*, 25 (1965) 1645.
- 3 R. M. ISMAIL, *Ger. P.* 1,210,849 (1963).
- 4 J. L. SPEIER, JR., *J. Am. Chem. Soc.*, 74 (1952) 1003.
- 5 J. L. SPEIER, JR., *U.S.P.* 2,611,778 (1952).
- 6 R. M. ISMAIL, *Helv. Chim. Acta*, 47 (1964) 2405.
- 7 R. M. ISMAIL, *Ger. P.* 1,182,232 (1963).

- 8 R. M. ISMAIL, *Z. Naturforsch.* 18b (1963) 582.
- 9 R. M. ISMAIL, *Austrian P.* 249,690 (1966).
- 10 K. A. ANDRIANOV AND G. YA. RUMBA, *Zh. obshch. Khim.*, 31 (1961) 4038.
- 11 B. RUSHTON, *J. Org. Chem.*, 30 (1965) 3988.
- 12 R. J. N. THIESSE, *Ger. P.* 1,163,824 (1964).

J. Organometal. Chem., 10 (1967) 421-426