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SEVERAL REACTIONS OF POLYHALOGENOPHENYLTRIMETHYLSILANES IN THE PRESENCE OF FLUORIDE ION

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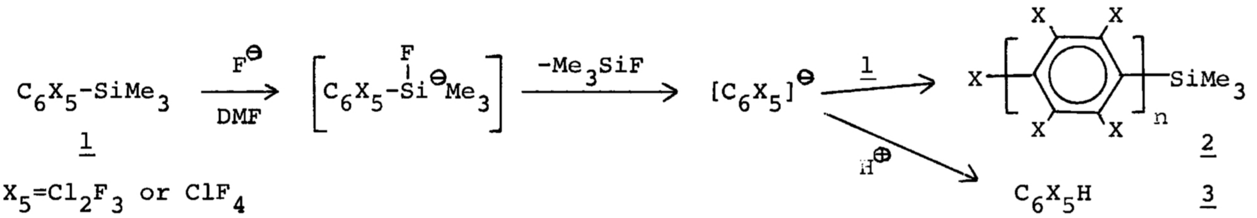
Polyhalogenophenyltrimethylsilanes such as 3,5-dichloro-2,4,6-trifluoro-, 3-chloro-2,4,5,6-tetrafluoro-, 2,6-difluoro-, and 2,6-dichlorophenyltrimethylsilanes in KF/DMF-system underwent Grignard-like reactions with benzaldehyde or iodine. In these reactions the silicon complex coordinated with fluoride ion was assumed to be the reaction intermediate.

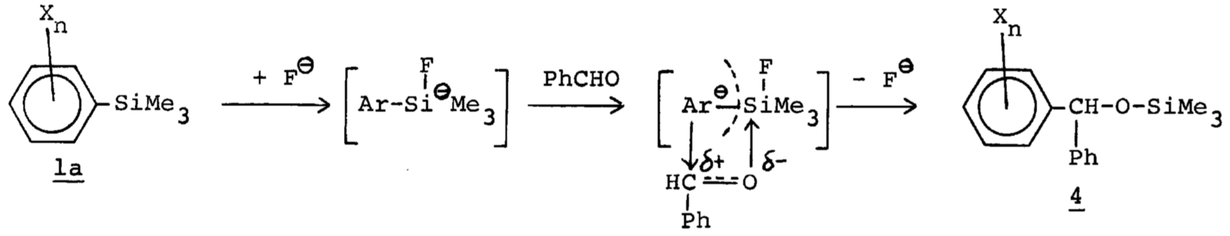
As we have reported previously[1)], (pentahalogenophenyl)trimethylsilanes [1] in dimethylformamide reacted very easily with potassium fluoride, and perhalogenopolyphenylenes [2] were formed by intermolecular elimination of trimethylfluorosilane. When a small amount of water was present in the reaction mixture, the trimethylsilyl group was replaced with hydrogen, giving pentahalogenobenzenes [3].



X_5=Cl_2F_3 or ClF_4

From the facts mentioned above, aryltrimethylsilane in KF/DMF-system appears to behave as a Grignard-like reagent, especially when the aryl ring carries strong electron-withdrawing groups. So we extended our investigation on the reactions of this kind. As a typical example of Grignard-like reaction, we chose that of (pentahalogenophenyl)trimethylsilanes with benzaldehyde. The similar reaction has been reported by H. Gilman et al. very recently[2)]. They carried out the reaction between pentafluoro-(or pentachloro-)phenyltrimethylsilane and benzaldehyde by heating them at 170°C for 4 days without solvent, and obtained 2,3,4,5,6-pentahalogenobenzhydryloxytrimethylsilane ; 4 (X_n=F_5 or Cl_5).

In our experiments in KF/DMF-system, the reaction between (pentahalogenophenyl)-trimethylsilane 1a (X_n=3,5-Cl_2-2,4,6-F_3 or 3-Cl-2,4,5,6-F_4) and benzaldehyde occurred exothermally even at room temperature. The starting aryltrimethylsilane disappeared in a few minutes (glc), and after the usual treatment the similar product 4 was obtained.



For example, into a solution of <u>1a</u>[X_n=Cl_2F_3] (5.46 g) and benzaldehyde (4.24 g) in DMF (20 ml), potassium fluoride (0.12 g) was added, and the whole was stirred for three hours at room temperature. The reaction mixture was poured into ice water and oily matter was extracted with ethyl ether. The extract was dried over magnesium sulfate, then distilled in vacuum. The fraction of bp 163-166°C/18 mmHg (5.12 g, 68%) was collected to give <u>4</u> [X_n=Cl_2F_3], which solidified to a crystalline mass of mp 46-48.5°C (Found: F, 15.0%. Calcd: F, 15.0%). The structure of the product was clear from the ^1H and ^{19}F NMR and IR spectra (<u>Table 1</u>).

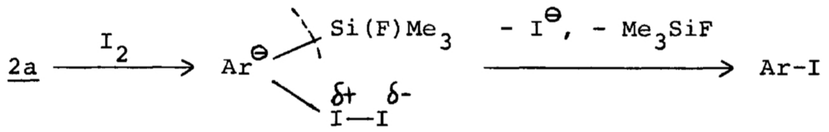
Table 1 Physical Data of Compound <u>4</u>

X_n	bp	Yield	NMR ^{19}F (δ ppm)*				NMR ^1H (τ)		IR (cm^{-1})		
	°C/mmHg	%	2F	4F	5F	6F	$SiMe_3$	CHO	$SiMe_3$	Si-O-C	C-F
3,5-Cl_2-2,4,6-F_3	132-135/2 (mp 49-50)	68	35.8 (d)	33.0 (t)	——	35.8 (d)	9.87	3.87	1255 840	1100 1028	1068
3-Cl-2,4-5,6-F_4	116-119/2	60	42.3 (d)	56.2 (dd)	86.4 (t)	58.6 (dd)	9.88	3.79	1260 845	1128 1030	1074
2,6-F_2	124-125/3	56	34.9 (t)	——	——	34.9 (t)	9.93	3.66	1256 841	1092 1028	1068
2,6-Cl_2	118-128/8	43	——	——	——	——	9.90	3.39	1253 839	1104 1031	——

* From ext. CF_3CO_2H

Not only (pentahalogenophenyl)trimethylsilanes, but 2,6-difluoro- and 2,6-dichlorophenyl compounds also reacted in the same manner. However, the other aryltrimethylsilanes, for example o-, m-, and p-fluoro- or p-nitrophenyl compounds, did not react at all under this condition. This is probably because the negativity of the single substituent on the aryl nucleus of these compounds is not enough to assist the formation of the corresponding aryl anion.

As another reaction of this kind, we examined iodination of polyhalogenophenyltrimethylsilanes. In this case too, they reacted with iodine in dimethylformamide at room temperature in the presence of potassium fluoride. Polyhalogenoiodobenzenes were obtained as the products, but the reactions were more sluggish and yields were poorer compared with those with benzaldehyde.



1) K.Kuroda and N.Ishikawa, Kogyo Kagaku Zasshi, <u>74</u>, 495(1971).

2) A.F.Webb, D.S.Sethi, and H.Gilman, J.Organometal.Chem., <u>21</u>, 61(1970).

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