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ORGANOSILICON COMPOUNDS
LXVIII*. ELECTROPHILIC CHLORINATION OF PHENYLFLUOROSILANES

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SUMMARY

We have studied the chlorination of the compounds $PhSiMe_{3-n}F_n (n=0\text{–}3)$ with ferric chloride or iodine as catalyst. The isomeric composition of the chlorination products and the extent of chloro- and iodo-desilylation has been determined, and the reactivities of the phenylfluorosilanes $PhSiMe_{(3-n)}F_n$ relative to benzene have been measured by the competition method.

INTRODUCTION

An investigation of electrophilic chlorination of phenylmethylchlorosilanes[2] showed that the trichlorosilyl group is *meta*-directing. A similar conclusion was reached for the analogous trifluorosilyl group by Ponomarenko[3], who in chlorination of phenyltrifluorosilane at 50° in the presence of ferric chloride obtained 18% of the *o*-, 79–82% of the *m*- and 0–3% of the *p*-chloro derivative. In chlorination of phenyltrimethylsilane under identical conditions he obtained 51% of the *o*-, 24% of the *m*-, and 25% of the *p*-chloro derivative. Thus, as expected from their inductive effects, the trifluorosilyl group is strongly *meta*-directing while the trimethylsilyl group is weakly *ortho-para*-directing.

We have now studied the chlorination of the series of phenylmethylfluorosilanes $C_6H_5Si(CH_3)_{3-n}F_n$ with $n=0\text{–}3$. The reaction conditions were identical with those used for chlorination of a series of phenylchlorosilanes[2], and also of benzylfluorosilanes[4], so that direct comparison is possible.

EXPERIMENTAL

Preparation of phenylfluorosilanes

The phenylfluorosilanes were prepared from analogous phenylchlorosilanes by Frost's method[5], and their physical constants are shown in Table 1.

Phenyltrifluorosilane. Antimony trifluoride (99 g, 0.56 mole) was slowly added

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* For Part LXVII see ref. 1.

TABLE 1

PHYSICAL CONSTANTS OF PHENYLFLUOROSILANES

Compound	B.p. (°C/mm)		n_D^{20}	d_4^{20}
	Found	Reference		
Phenyltrifluorosilane	100.8/760	101.8/760[6]	1.4555	1.2996
Phenyldifluoromethylsilane	139–141/760	143/767[7]	1.4599	1.1053[a]
Phenylfluorodimethylsilane	160–161.5/760	162.4/760[9]	1.4775	1.0074

[a] Lit.[8] d_4^{20} 1.0993.

with continuous stirring and cooling (0–5°) to 106 g (0.5 mol) of phenyltrichlorosilane and 22 ml of antimony pentachloride. The mixture was then refluxed for about 2 h. Distillation and subsequent rectification on a glass column filled with cantal loops (60 cm length, 20 TL) yielded 43 g (53%) of phenyltrifluorosilane.

Phenylmethyldifluorosilane. Phenylmethyldifluorosilane (114.6 g, 0.6 mole), 22 ml antimony pentachloride and 84.2 g (0.475 mole) antimony trifluoride similarly gave 21 g (22%) of phenylmethyldifluorosilane.

Phenyldimethylfluorosilane. Phenyldimethylchlorosilane (153 g, 0.9 mole) 22 ml antimony pentachloride and 59 g (0.33 mole) antimony trifluoride similarly gave 23 g (16.5%) of phenyldimethylfluorosilane.

Phenyltrimethylsilane and o-, m- and p-chlorophenyltrimethylsilanes. These were prepared in the usual way[2].

The purity of all the compounds used was checked by gas chromatography with a thermally-conductivity detector. Silicone elastomer E 302 was used on a packing of Chromosorb (100/200 mesh).

Chlorination of phenylfluorosilanes

The chlorination of phenylfluorosilanes was carried out as previously described for phenylchlorosilanes[2]. The reaction temperature was maintained at 60±2° and the degree of conversion was kept between 3 and 8%. The amount of catalyst (ferric chloride or iodine) represented 3 mole%. The maximum admissible amount of dichlorophenyl derivatives was 3% of the monochlorophenyl derivatives. The amount of *o*-, *m*- and *p*-dichlorobenzene formed by chlorine cleavage of the corresponding isomers of the (monochlorophenyl)silicon compounds was somewhat greater than from the analogous phenylchlorosilanes, but still insignificant in comparison with the amount of monochlorophenyl derivatives formed.

Some chlorinations were repeated 2–3 times under the same conditions. The reproducibility was roughly the same for all the isomers and for chlorobenzene, being between 2 and 5%. For some of the phenylfluorosilanes the extent of chlorodesilylation or iododesilylation reaction was also determined.

Determination of the relative rates of chlorination of phenylfluorosilanes

The competition method was used, with bromobenzene and cumene as standards. The reactivities are given relative to that of benzene. Reactions were carried out at 60±2°, with the catalyst iron present to the extent of 3 mole% of the sum of the standard plus phenylsilane. The mixture was analyzed and the relative rate constants were calculated as before[2]. Because of the great differences in the reactivities we could not satisfactorily measure the relative reactivities of phenylmethyldifluorosilane and cumene, and the reactivity of this fluorosilane relative to benzene has been calculated only from the comparison of its reactivity with that of bromobenzene. In all cases the degree of conversion of each of the starting compounds was kept below 3–5%. The reactivities of individual positions of the benzene ring in phenylfluorosilanes were calculated as described by Ingold[10].

RESULTS AND DISCUSSION

Orientating effects of the methylfluorosilyl groups

Experimental results are given in Table 2. For the reactions catalysed by ferric chloride the results show trends similar to those for phenylmethylchlorosilanes. Thus the change from phenyltrimethylsilane to phenyldimethylfluorosilane is accompanied by a change from *ortho-para*-orientation to a weak *meta*-orientation, attributable to the increasing $-I$ effect of the silyl substituents. The changes on going to the other two members of the fluorosilane series are more pronounced than with the analogous chlorosilanes (*i.e.* the ratio $(o+p)/m$ decreases more steeply) and hence the trifluorosilyl group has, because of its more significant $-I$ effect, a more pronounced *meta*-directing influence than the trichlorosilyl group. Also the o/p ratio shows a steeper rise than in the chlorosilane series. The $-M$ effect of the trifluorosilyl group[11] is partly responsible, but another factor is that the smaller steric requirements of fluorine compared with chlorine result in less hindrance to substitution at the *ortho*-position.

TABLE 2

YIELDS (MOLE %) OF SUBSTITUTION AND CLEAVAGE PRODUCTS IN CHLORINATION OF PHENYLMETHYLFLUOROSILANES AT 60±2° WITH 2 MOLE % CATALYST

Compound	o	m	p	o/p	p/m	$(o+p)/m$	$o+m+p$	C_6H_5Cl	C_6H_5I
$FeCl_3$ as catalyst									
$C_6H_5Si(CH_3)_3$	46.9	30.5	22.6	2.12	0.74	5.28	52.8	47.2	
$C_6H_5Si(CH_3)_2F$	41.9	47.0	11.1	3.78	0.24	1.13	53.0	47.0	
$C_6H_5Si(CH_3)F_2$	36.2	58.7	5.1	7.10	0.09	0.70	50.2	49.8	
$C_6H_5SiF_3$	26.6	71.8	1.6	16.64	0.02	0.39	96.5	3.5	
I_2 as catalyst									
$C_6H_5Si(CH_3)_3$	45.8	24.5	29.7	1.54	1.21	3.08	31.7	49.6	18.7
$C_6H_5Si(CH_3)_2F$	54.0	42.0	4.0	13.50	0.09	1.38	46.0	30.1	23.9
$C_6H_5Si(CH_3)F_2$	85.4	8.9	5.7	15.00	0.64	10.23	50.8	37.9	11.3
$C_6H_5SiF_3$	41.9	54.6	3.5	12.00	0.06	0.83	92.0	3.5	4.5

With iodine as catalyst the changes in orientation are irregular, and difficult to interpret at present.

Cleavage reactions

In the phenylmethylfluorosilane series, the amount of chlorodesilylation is practically identical with all the three first members of the series, but phenyltrifluorosilane undergoes much less cleavage than these three or than phenyltrichlorosilane[2]. In contrast with the results for phenylmethylchlorosilanes, chlorodesilylation is more extensive with ferric chloride than with iodine as catalyst.

Effect of structure on the reactivity of phenylmethylfluorosilanes

The results summarized in Table 3 show that the phenylmethylfluorosilanes are somewhat less reactive than the corresponding phenylmethylchlorosilanes. This is in agreement with the larger $-I$ effect of fluorine than of chlorine. This causes the variation of log k/k_B with the number of halogen atoms to be more marked than in the phenylmethylchlorosilanes[2] (Fig. 1). The effects of additional fluorine atoms on log k/k_B are roughly additive, with the greatest difference occurring between the third and fourth member of the series, as with phenylmethylchlorosilanes.

TABLE 3

REACTIVITIES RELATIVE TO BENZENE OF PHENYLMETHYLFLUOROSILANES IN CHLORINATION AT 60±2° WITH 3 MOLE % IRON AS CATALYST

Compound	k/k_B	k/k_B	log k/k_B	Reactivity of position		
				o	*m*	*p*
$C_6H_5Si(CH_3)_3$	6.02[a]	6.02	0.780	8.38	5.33	8.70
$C_6H_5Si(CH_3)_2F$	0.702[a], 0.558[b]	0.63	−0.200	0.79	0.89	0.42
$C_6H_5Si(CH_3)F_2$	0.0966[b]	0.097	−1.015	0.105	0.17	0.03
$C_6H_5SiF_3$	0.0065[b]	0.0065	−2.187	0.0054	0.014	0.0002

[a] Calculated via cumene. [b] Calculated via bromobenzene.

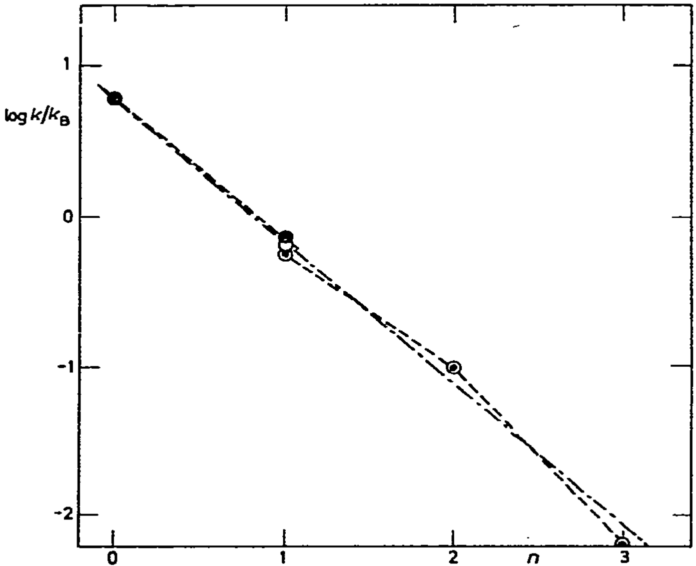

Fig. 1. Dependence of the logarithm of the relative rates of ferric chloride catalysed chlorination on the number of fluorine atoms in phenylmethylfluorosilanes. Internal standard: ● cumene, ⊙ bromobenzene (○ average value).

It is noteworthy that the reactivity of phenylmethylfluorosilanes is significantly lower than that of analogous benzylmethylfluorosilanes[4]. As with the phenylmethylchlorosilanes, the relatively low reactivities of phenylmethylfluorosilanes would not be expected for operation only of inductive effects of the silyl groups, but can be explained in terms of $(p \rightarrow d)\pi$-bonding in the phenyl–silicon bond.

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