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ORGANOSILICON COMPOUNDS
LXIX*. ELECTROPHILIC CHLORINATION OF BENZYLFLUOROSILANES

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SUMMARY

The orientating effects of silylmethyl groups of the type $(CH_3)_{3-n}F_nSiCH_2-$ ($n=0$–3) in electrophilic chlorination of $C_6H_5CH_2(CH_3)_{3-n}SiF_n$ have been measured. Ferric chloride and iodine were used as catalysts. All the groups are *o*- and *p*-directing, and this is explained in terms of hyperconjugation between the methylene hydrogens and the aromatic ring.

The competition method was used to determine the reactivities of these compounds relative to benzene. With the exception of the compound with $n=3$, the members of the series are more reactive than benzene. The reactivities are interpreted mainly in terms of the inductive effects of the silylmethyl groups, though these may be modified by $(p\rightarrow d)$ interaction in the Si–F bonds.

INTRODUCTION

We have previously studied the effects of the substituents[2], on reactivity and orientation in catalysed electrophilic chlorination of ZC_6H_5 compounds, where $Z=Me_{(3-n)}Cl_nSiCH_2$ or $Me_{(3-n)}X_nM$, with $n=0$–3, M=Si or Ge, X=Cl or F[1–4]. We now describe a similar study of the effects of $(CH_3)_{3-n}F_nSiCH_2-$ ($n=0$–3) groups. Cleavage of the Si–C bonds would not be expected to occur during chlorination[5].

EXPERIMENTAL

Preparation of benzylfluorosilanes

All the benzylfluorosilanes were prepared from benzylchlorosilanes by Frost's method[7].

Benzyltrifluorosilane. 123 g (0.66 mol) SbF_3 were gradually added with vigorous stirring and cooling to +5° to a mixture of 136 g (0.6 mol) benzyltrichlorosilane and 22 ml $SbCl_5$. The mixture was then refluxed for 2 h. Distillation yielded 60 g

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* For part LXVIII see ref. 1.

(56%) of benzyltrifluorosilane boiling between 134 and 135.5°. (Found: F, 32.40. $C_7H_7F_3Si$ calcd.: F, 32.35%.)

Benzylmethyldifluorosilane. This (67%) was prepared analogously, but with cooling to 0°, the reaction being more vigorous. The b.p. was 167.5–168.5°; n_D^{20} 1.4593, d_4^{20} 1.0864. (Found: F, 22.23. $C_8H_{10}F_2Si$ calcd.: F, 22.06%.)

Benzyldimethylfluorosilane. This (37%) was obtained analogously b.p. 183–184°. (Found: F, 11.42. $C_9H_{13}FSi$ calcd.: F, 11.29%.)

(Chlorobenzyl)trimethylsilanes

The synthesis of (chlorobenzyl)trimethylsilanes required for estimation of the elution volumes in chromatographic analysis of the mixture has been described before[4].

The purity of all compounds used for kinetic measurements was checked chromatographically[4].

Methods for determination of orientating effects

A flat chlorination flask of about 10 ml capacity with a weighed amount of catalyst (either iron powder or iodine) and of the substrate was brought to the required temperature and dry chlorine gas was introduced at a rate of 10 ml/min. The flow of chlorine was stopped before the conversion to monochloro derivatives exceeded 5–8%. After cooling, the mixture was methylated with an excess of methylmagnesium bromide and then hydrolyzed with dilute hydrochloric acid. The ether layer was then dried with calcium chloride and ether distilled off. A more detailed account of this procedure is given in ref. 2.

The GLC analysis was carried out as described for benzylchlorosilanes[4].

Methods for determination of the relative rate constants

Relative reactivities were studied by the competition method with the apparatus and the conditions used for the determination of orientating influences (reaction temperature 60°, concentration of catalyst 3%). The conversion was not allowed to exceed 5%. Further details are given in refs. 2 and 4. Because of their suitable elution volumes and reactivities, tert-butylbenzene and benzene were used as standards, and the relative reactivities of tert-butylbenzene and benzene were determined under the conditions of our chlorinations. The reactivities of the individual positions of the atomatic ring are based on a value of 6 for the overall reactivity of benzene.

RESULTS AND DISCUSSION

Orientation effects of (methylfluorosilyl)methyl groups

The compositions of the reaction products expressed are shown for both catalysts in Table 1. Deviations from the average values were 1.5–5 rel.% for *o*- and *p*-isomers, but 25 rel.% for the *m*-isomer which was present in very small quantities. The possible dependence on the amount of catalysts or on the reaction temperature was not examined, it being assumed that both these factors would have no significant effect as was the case with benzyltrimethylsilane and benzyldimethylchlorosilane[4].

Table 1 shows that all the silylmethyl groups have a pronounced *o,p*-directing

TABLE 1

DISTRIBUTION OF THE ISOMERS DURING CHLORINATION OF BENZYLMETHYLFLUOROSILANES

Temperature 60°, catalyst concentration 3%.

Compound	Distribution of isomers (% $\pm\varepsilon$[a])			Ratio p/o
	Ortho	*Meta*	*Para*	
Catalyst I_2				
$C_7H_7(CH_3)_3Si$[4]	28.1 ± 5.0	0	71.9 ± 1.9	2.56
$C_7H_7(CH_3)_2SiF$	41.8 ± 2.1	0	58.2 ± 1.5	1.39
$C_7H_7(CH_3)SiF_2$	48.5 ± 0.4	0	51.5 ± 0.3	1.06
$C_7H_7SiF_3$	45.9 ± 2.7	3 ± 25	51.1 ± 2.4	1.11
Catalyst $FeCl_3$				
$C_7H_7(CH_3)_3Si$[4]	34.1 ± 2.3	0	65.9 ± 1.1	1.93
$C_7H_7(CH_3)_2SiF$	40.2 ± 0.3	0	59.8 ± 0.2	1.49
$C_7H_7(CH_3)SiF_2$	42.7 ± 1.9	0	57.3 ± 1.4	1.34
$C_7H_7SiF_3$	49.6 ± 1.9	5 ± 25	45.4 ± 2.1	0.92

[a] $\varepsilon = \frac{\Delta X}{X} \cdot 100$ (%).

effect, the *para-* being more activated than the *ortho*-position. The *meta*-isomer is formed only in a small amount from benzyltrifluorosilane. When using ferric chloride as catalyst, the $\%p/\%o$ ratio decreases regularly with increasing number of fluorine atoms on the silicon atom; when using iodine, there is a steeper decrease at first, followed by a rise of the p/o ratio to the last member of the series. The range of the p/o values is greater than for benzylchlorosilanes (2.56–1.54 for chlorosilanes catalyzed by iodine as compared with 2.56–1.11 for fluorosilanes, and 1.93–1.22 for catalysis by $FeCl_3$, as compared with 1.93–0.92).

The marked *o,p*-orientation for the first three members of the series can be explained by operation of the $+I$ effect, which activates mainly the *ortho* and *para* positions. With the last member, benzyltrifluorosilane, which is comparable in reactivity with benzene, this explanation fails. As with benzylchlorosilanes, the explanation can be found in the role of hyperconjugation of methylene hydrogens with the aromatic system, which might account for the fact that the p/o ratio in a number of cases is greater than would be predicted statistically. The greater $-I$ effect of fluorine than of chlorine [σ_I(Cl) 0.47, σ_I(F) 0.52][6] will bring about a lower activation of the *para-* than of the *ortho*-position[8]. There should thus be a lower p/o ratio for benzylfluorosilanes than for benzylchlorosilanes, as observed. The p/o ratio may also be, however, affected by the smaller steric screening of the *o*-position by fluorine atoms as compared with the chlorine atoms.

Effect of structure on the reactivity of benzylfluorosilanes

The relative rate constants of benzylmethylfluorosilanes and the reactivities of the individual positions of the ring are shown for both catalysts in Table 2. All the compounds, except for benzyltrifluorosilane in the reaction catalysed by $FeCl_3$, are more reactive than benzene. All the benzylfluorosilanes displayed higher reactivities with iodine than with ferric chloride as catalyst. The span of reactivities between

TABLE 2

RATE CONSTANTS OF BENZYLMETHYLFLUOROSILANES
Temperature 60°, catalyst concentration 3%.

Compound	Standard	$k_{rel} \pm \varepsilon^a$	k/k_B^b	Reactivity of position		
				Ortho	*Meta*	*Para*
Catalyst I_2						
$C_7H_7(CH_3)_3Si$[4]	p-$(i$-$C_3H_7)_2C_6H_4$	20.15 ± 4.8	3870	3260	0	16700
$C_7H_7(CH_3)_2SiF$	t-$(CH_3)_3CC_6H_5$	14.2 ± 6.0	421	528	0	1470
$C_7H_7(CH_3)SiF_2$	t-$(CH_3)_3CC_6H_5$	1.20 ± 3.1	35.7	52	0	110
$C_7H_7SiF_3$	t-$(CH_3)_3CC_6H_5$	0.0721 ± 11.5	2.14	2.95	0.19	6.58
Catalyst $FeCl_3$						
$C_7H_7(CH_3)_3Si$[4]	p-$(i$-$C_3H_7)_2C_6H_4$	37.7 ± 15	1800	1840	0	7130
$C_7H_7(CH_3)_2SiF$	t-$(CH_3)_3CC_6H_5$	15.2 ± 4.2	169	204	0	606
$C_7H_7(CH_3)SiF_2$	t-$(CH_3)_3CC_6H_5$	1.28 ± 9.2	13.5	17.3	0	46.4
$C_7H_7SiF_3$	t-$(CH_3)_3CC_6H_5$	0.0867 ± 10	0.997	1.48	0.15	2.72
	C_6H_6	1.08 ± 8.4				

[a] $\varepsilon = \frac{\Delta k_{rel}}{k_{rel}} \cdot 100\ (\%)$. [b] Relative rate constant referred to benzene.

the first and the last member of the series is greater than with benzylchlorosilanes[4], and the curves relating $\log(k/k_B)$ to the number of fluorine atoms are linear (Fig. 1). The reactivities of the second and third members of the fluorosilane series are greater than the reactivities of the corresponding members of the chlorosilane series. The drop of reactivity on replacing one methyl with fluorine is less in the first three members of the series than with the chloro derivatives (1.24 for $FeCl_3$ and 1.14 for iodine)[4] and, in terms of $\log(k/k_B)$, is approximately equal to 1.06 for $FeCl_3$ and to 1.02 for iodine. Since fluorine is more electronegative than chlorine, the decrease of

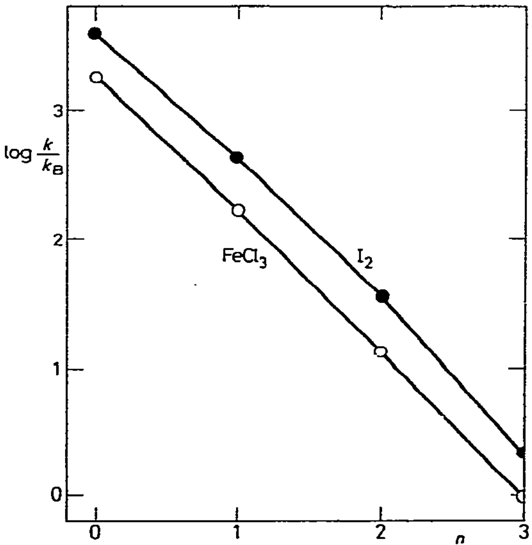

Fig. 1. Dependence of log (k/k_B) on the number of fluorine atoms in the molecule of the $C_7H_7(CH_3)_{3-n}$-SiF_n series.

reactivity caused by replacement of methyl with fluorine should be slightly greater than that with chlorine. A plot of log (k/k_B) against σ^* (*cf.* ref. 9) is not linear (Fig. 2), the reactivity being unexpectedly low with the last member of the series. [An experimental value of σ^* for the trifluoromethyl group is not available, but a value can be calculated from the formula[9] $\sigma^*(X) = 2.8\ \sigma^*(CH_2X)$.] Since the mono- and difluoro-substituted benzylsilanes are more reactive than the corresponding chlorosilanes, and since the decrease of reactivity between the first and second and between the second and third member of the fluorosilane series is less than that in the chlorosilane series, it seems that the inductive effect of fluorine is partly offset by a $(p\rightarrow d)\pi$ interaction between fluorine and silicon. The lower reactivity of benzyltrifluorosilane than of benzyltrichlorosilane can be attributed to the fact that such $(p\rightarrow d)\pi$ bonding will be less important when three fluorine atoms are bound to one silicon.

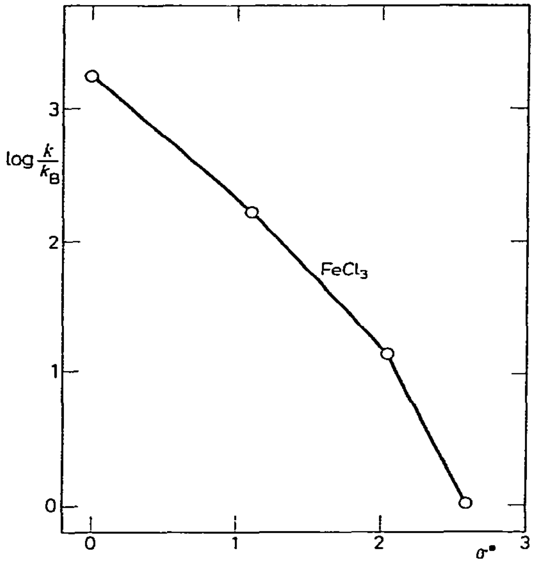

Fig. 2. Correlation of log (k/k_B) of the $C_7H_7(CH_3)_{3-n}SiF_n$ series and σ^* of the $-CH_{3-n}F_n$ groups.

Although other effects are clearly of significance, we conclude that the reactivity of the compounds investigated is mainly determined by the influence of the inductive effects of the silylmethyl groups.

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