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THE THIOLATE ANION AS A NUCLEOPHILE
PART I. REACTIONS WITH HEXAFLUOROBENZENE, DECAFLUOROBIPHENYL AND HEXACHLOROBENZENE

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SUMMARY

The nucleophilic substitution of hexafluorobenzene, decafluorobiphenyl, and hexachlorobenzene with the thiolate anion, RS^- ($R = H$, Me, Et, Ph, C_6F_5) has been studied. Compounds of the type C_6F_5SR, $C_6(SR)_2F_4$, $C_6F_2(SR)_4$, $RSC_6F_4{\cdot}C_6F_4SR$, $(RS)_3F_2C_6{\cdot}C_6F_2(SR)_3$, $C_6(SR)_2Cl_4$, and $C_6Cl_2(SR)_4$ were isolated as major products. The new compounds were characterized by elemental analysis, infrared, Raman, mass and NMR spectra.

INTRODUCTION

Halogenated aromatic nuclei are susceptible to nucleophilic attack, and this type of reaction has been widely studied with a variety of nucleophiles[1]. Sulfur-containing nucleophiles of the type RS^- have been somewhat neglected. Nucleophilic substitution of hexafluorobenzene with the hydrogen sulfide anion, HS^-, and the thiophenolate anion, PhS^-, has been examined[2,3] and yielded pentafluorothiophenol and 1,2,4,5-tetrafluoro-bis-phenylthiobenzene or 1,4-difluoro-tetrakis-phenylthiobenzene respectively. Substitution of hexachlorobenzene with various sulfur-containing nucleophiles, but not the methylthiolate anion, has been studied[4]. In continuing our studies on sulfur-containing derivatives of hexafluorobenzene[5] the nucleophilic substitution of hexafluorobenzene, decafluorobiphenyl, and hexachlorobenzene with the thiolate nucleophiles RS^-, where $R = H$, Me, Et, Ph, and C_6F_5, has been examined. The results are summarized in the equations shown below, where the major products only are indicated.

$C_6F_6 + HS^- \rightarrow C_6F_5SH$ + perfluoropoly(phenylene sulfide)
$C_6F_6 + MeS^- \rightarrow C_6F_5SMe, C_6F_4(SMe)_2, C_6F_2(SMe)_4$
$C_6F_6 + EtS^- \rightarrow C_6F_5SEt, C_6F_4(SEt)_2, C_6F_2(SEt)_4$

$C_6F_6 + PhS^- \rightarrow C_6F_4(SPh)_2$

$C_6F_6 + C_6F_5S^- \rightarrow$ perfluoropoly(phenylene sulfide)

$C_6F_5{\bullet}C_6F_5 + MeS^- \rightarrow MeSC_6F_4{\bullet}C_6F_4SMe, (MeS)_3C_6F_2{\bullet}C_6F_2(SMe)_3$

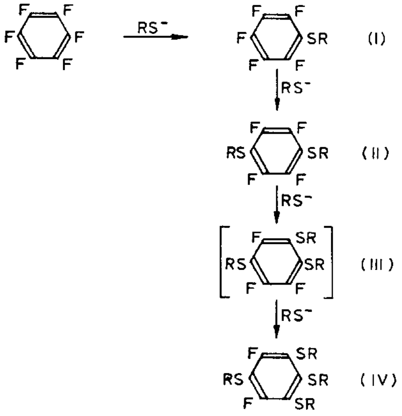
$C_6F_5{\bullet}C_6F_5 + EtS^- \rightarrow EtSC_6F_4{\bullet}C_6F_4SEt$

$C_6F_5{\bullet}C_6F_5 + PhS^- \rightarrow PhSC_6F_4{\bullet}C_6F_4SPh$

$C_6Cl_6 + MeS^- \rightarrow C_6Cl_4(SMe)_2, C_6Cl_2(SMe)_4$

RESULTS AND DISCUSSION

In the above reactions the derivatives formed from hexafluorobenzene are primarily mono(I)-, di(II)-, or tetra(IV)-substituted.



No evidence for tri-, penta-, or hexa-substituted products was obtained. The yield of the monosubstituted product was usually relatively small, as it appeared to react with the nucleophile as readily, or more readily than hexafluorobenzene, forming the disubstituted product (II). It was not possible to isolate a monosubstituted product when hexachlorobenzene was treated with a variety of thiolate nucleophiles and only the di- and tetra-substituted products were isolated[4]. The orientation of the disubstituted product was undoubtedly *para*-SR. In no case could a trisubstituted product having a structure similar to (III) be isolated. In the, presumably, very rapid conversion of (III) → (IV) it appears that the orientatating effect of the fluorine is predominant as the group enters at a position *ortho* to one fluorine and *para* to the other. In the conversion (I) → (II), however, the main orientation is caused by the –SR group giving substitution *para* to it. The penta- and hexa-substituted products may be sterically hindered, rendering their preparation extremely difficult. Previous work indicates that the structure of (IV) should contain a *para*-fluorine[3]. However, the NMR spectra reported here indicate that in (IV) the two fluorine atoms are *meta* relative to each other.

When the hydrogen sulfide anion, HS^-, was used as a nucleophile with hexafluorobenzene the thiol formed, C_6F_5SH, also acted as a nucleophile in the basic solution. No dithiols were isolated from this reaction and perfluoropoly-

(phenylene sulfide) was formed, presumably as the result of an attack of the $C_6F_5S^-$ nucleophile on the C_6F_5 nucleus of another $C_6F_5S^-$ anion[2]. This reaction was studied under argon, so that atmospheric oxidation of the thiol or the thiolate ion could not be involved as an initial step in the reaction. When the pentafluorothiophenolate anion was used as a nucleophile, as in the reaction with hexafluorobenzene, it reacted primarily with itself and not with hexafluorobenzene as perfluoropoly(phenylene sulfide) was the only product isolated.

All the reactions were rapid and carried out in a refluxing mixture of approximately two parts of pyridine and one part of ethylene glycol. The mechanism of the reaction probably involves some weak complex formation between the hexafluorobenzene and the pyridine, with the nucleophile displacing the pyridine from the complex. Hexafluorobenzene is known to form a weak complex with benzene[6]. Analysis of a equi-molecular mixture of hexafluorobenzene and methylthiolate anion showed that after 2 min about 50% of the hexafluorobenzene (detected quantitatively by VPC) had reacted, and that very little reaction occurred subsequently. Two minutes was the minimum time necessary for efficient mixing to occur in the experimental technique used in this study.

The actual products isolated depended on the stoichiometry of the reactants. It must be stressed that only the major products have been isolated. TLC of the crude products usually showed at least one minor product together with the major product(s).

The spectra of the compounds isolated have been examined in an attempt to determine their structures. The NMR spectra, detailed in Table 1, were valuable in assigning the structures. It has been observed that the proton NMR signal of an $-XMe$ ($X = O, N, S$) group in polyfluoroaromatics is split into a triplet due to coupling with fluorines *ortho* to it[7]. In C_6F_5SMe this coupling is reported as 0.7 Hz[7]. In disubstituted polyfluoroaromatic compounds, such as *p*-$MeSC_6F_4$-OMe, the extent of this coupling is considerably reduced[7].

The orientation of the compound $C_6F_4(SMe)_2$ is likely to be *para*-SMe, as further nucleophilic substitution of C_6F_5SMe with the methoxide anion gives *p*-$MeSC_6F_4OMe$[3]. The compound *p*-$C_6(SMe)_2F_4$ has been reported[8], but not fully characterized by elemental analysis. The proton NMR spectrum contained a singlet, showing no coupling, although the half-peak width was about 2 Hz. The ^{19}F spectrum was also a singlet. This result would be expected if the SMe groups were *para* and all the fluorines are equivalent. The orientations of the other $C_6(SR)_2F_4$ compounds are assumed by analogy to be *para*-SR. The compounds $C_6(SPh)_2F_4$ and $C_6(SCH_2CH_2OH)_2Cl_4$ have been shown by chemical degradation to be *para*-SR[3, 4].

The proton NMR spectrum of $C_6F_2(SMe)_4$ was measured at -15°, 36–7°, and 70° and always appeared superficially to be a triplet. It is, in fact, assumed to consist of three singlets of intensity ratio 1:2:1, indicating *meta*-fluorines. If the orientation of the fluorines is *meta* then there are three different SMe groups;

TABLE 1

NMR SPECTRA

Compound	Solvent	$^1H^a$		^{19}F	
		$\delta(\tau)$	J(Hz)	δ^b(ppm)	Instrument^f
C_6F_5SH	CCl_4	7.523(t)	0.75	see Ref. 5	
$C_6F_4(SMe)_2$	$CDCl_3$	7.495(s)	—	134.67^c(s)	A
				(135.3^d)	
$C_6F_4(SPh)_2$	$CDCl_3$			131.67^c(s)	A
$C_6F_2(SMe)_4$	$CDCl_3$	7.498(s)^g		99.95^c(s)	A
		7.483(s)^g	Ratio		
		7.468(s)^g	1:2:1		
$HSC_6F_4•C_6F_4SH$	$(CD_3)_2CO$	5.742(s)		137.6(m)	B
				139.4(m)	
$MeSC_6F_4•C_6F_4SMe$	$CDCl_3$	7.367(t)	1.1	134.46^c(m)	C
				138.36^c(m)	
$(MeS)_3C_6F_2•C_6F_2(SMe)_3$	$CDCl_3$	7.635(d)	1.0	101.69^{c,e}(d)	C
		7.485(d)	1.8	106.61^{c,e}(d)	
		7.398(d)	2.0		
$C_6Cl_4(SMe)_2$	CCl_4	7.510(s)			
$C_6Cl_2(SMe)_4$	CCl_4	7.527(s)			

s = singlet, d = doublet, t = triplet, m = multiplet

[a] Measured on a Varian A60, except C_6F_5SMe (Varian HA100).

[b] Measured from $CFCl_3$ as internal standard.

[c] Corrected from CF_3CO_2H as external standard.

[d] See Ref. 8

[e] Coupling constants 14.2 Hz (101.69 ppm), 16.9 Hz (106.61 ppm).

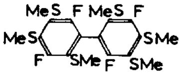
[f] A = Bruker HX60, B = Varian HA56/60, C = Jeol C6OHL.

[g] At −15°; 7.514, 7.496, 7.481 τ (Varian A60 - CCl_4); at 36–7°; 7.530, 7.514, 7.498 τ (Varian A60 - CCl_4); at 70°; 7.550, 7.532, 7.518 τ (Varian A60 - CCl_4).

one *ortho* to both fluorines, one *meta* to both fluorines, and two *ortho* to one fluorine and *para* to the other. If the fluorines were *para*, as might be expected from previous work on similar systems[3], all the SMe groups should be equivalent. The measurements at variable temperature eliminate the possibility of the spectrum arising from rotational effects in a symmetrical structure. If the fluorines were *ortho* there should be two non-equivalent SMe groups. The ^{19}F spectrum appears as a singlet at 99.45 ppm with half-peak width of about 5 Hz. Higher resolution shows that this peak is split, but that the coupling constant is less than 1 Hz.

This data, the low chemical shift and small coupling constant are similar to those observed in *m*-$C_6F_2H_4$[9] and confirm that the fluorines are *meta* in $C_6F_2(SMe)_4$. The orientation of $C_6F_2(SPh)_4$, which could not be isolated in the present work, was deduced from Raney nickel reduction and oxidation to be *para*-fluorine. The validity of the oxidative procedure is, however, somewhat in doubt as the product was not characterized[3]. The structures of the compounds $C_6Cl_2(SR)_4$, obtained from nucleophilic substitution of hexachlorobenzene, were arbitrarily assumed to be *para*-chlorine[4].

The orientation of $MeSC_6F_4{\bullet}C_6F_4SMe$ is 4,4′. The proton NMR spectrum is a triplet, as expected, which becomes a singlet when the fluorine is decoupled and the melting point is identical with that of a sample prepared from 4,4′-dimercapto-octafluorobiphenyl[10]. The ^{19}F spectra of the thiol and of the methylthio derivative were very similar, both being two distinct multiplets, and are as predicted for 4,4′-octafluorobiphenyl derivatives. The orientation of the other compounds, $RSC_6F_4{\bullet}C_6F_4SR$, is also assumed to be 4,4′. The proton NMR spectrum of $(MeS)_3F_2C_6{\bullet}C_6F_2(SMe)_3$ contained three doublets with coupling constants 2.0, 1.8, and 1.0 Hz, which, when the fluorine is decoupled, exhibited three triplets of equal intensity. Although free rotation about the bond between the rings is not possible due to steric hindrance, if it is assumed that no interaction between the two rings occurs the structure shown is as predicted from the proton NMR spectrum.



The fluorine NMR spectrum consists of two doublets which may be explained from the basis of some interaction between the fluorine atoms across the rings.

The proton NMR spectra of $C_6Cl_4(SMe)_2$ and $C_6Cl_2(SMe)_4$ were singlets both of half-peak width about 0.5 Hz, and, as expected, showed no chlorine–hydrogen coupling.

The infrared and Raman spectra [the latter were recorded only for $C_6(SMe)_2F_4$ and $C_6F_2(SMe)_4$] showed characteristic peaks for the substituent R and for the carbon–carbon–carbon ring vibrations. The carbon–fluorine frequencies were found to be a characteristic of the degree of substitution and may be used to infer the degree of substitution. In C_6F_5SMe the C–F bands were observed at 1090, 984–961, and 862 cm^{-1}, in $C_6(SR)_2F_4$ at 1240 ± 3, 952 ± 10, and 813 ± 1 cm^{-1} and in $C_6F_2(SR)_4$ at 968 ± 10 and 847 cm^{-1}; there were coincident bands in all the spectra at 1161 ± 2 and 1229 ± 3 cm^{-1} respectively. The $S{-}CH_3$ frequency in $C_6F_2(SMe)_4$ and $C_6(SMe)_4F_2$ may be assigned to a strong Raman line, with no infrared counterpart, at 700 cm^{-1}, and the S–C(ring) is found in the Raman spectra at 517 ($C_6(SMe)_2F_4$) and 470 cm^{-1} ($C_6F_2(SMe)_4$).

A change in absorption as the substitution of the nucleus changes also occurs in the UV–visible spectra. In the series C_6F_6, C_6F_5SMe, $C_6F_4(SMe)_2$ and $C_6F_2(SMe)_4$ the following changes were observed (wavelengths in nm, followed by molar extinction coefficients): $^1B_{1u} \leftarrow {}^1A_{1g}$, 203(3.38), 216(3.57), 214(4.04), 229 (4.43); $^1B_{2u} \leftarrow {}^1A_{1g}$, 220 (3.16), 242 (3.40), 243(3.50), 274(4.33) respectively.

Examination of the dipole moments was inconclusive. It is known that benzene, the solvent employed, and hexafluorobenzene form a 1:1 complex[6], and as the dipole moments of C_6F_5SMe (2.71 D), $C_6F_4(SMe)_2$ (2.77 D), and $C_6F_2(SMe)_4$ (3.05 D) are all very similar it is assumed that they also form complexes with benzene.

The mass spectra of the compounds have been examined, and all confirmed the molecular weights. The methyl compounds $C_6F_4(SMe)_2$ and $C_6F_2(SMe)_4$ were studied in more detail and showed peaks characteristic of the loss of the methyl group at M − 15 and M − 30, and M − 15, M − 30, M − 45, and M − 60 respectively. There are no peaks corresponding to the loss of fluorine or sulfur from the molecular ion at M − 19 or M − 32, but subsequent fragments may decompose by loss of fluorine or sulfur. Both spectra show a major peak at $m/e = 45$ corresponding to $CHS^{\bullet +}$ (mass measurement on a photoplate shows a major peak at $m/e = 44.9813$ or 44.9798 corresponding to m/e at 44.9798 for $CHS^{\bullet +}$), as would be expected in the decomposition of methylthio ethers.

EXPERIMENTAL

Most reagents were available commercially. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, West Germany. The analytical data and physical properties of some of the compounds prepared are shown in Table 2. The infrared spectra were recorded on a Perkin–Elmer 457 spectrophotometer as mulls with Nujol or hexachlorobutadiene, or as KBr discs. The UV–visible spectra were recorded in methanol solution on a Coleman 124 double-beam ultraviolet spectrophotometer. Mass spectra were recorded on a DuPont 21–110B high-resolution mass spectrograph or a DuPont 21–491 mass spectrograph. Raman spectra were recorded on a Coderg PHO Raman spectrograph using a Coherent Radiation M.G. 52 ion laser. Dipole moments were measured in benzene solution on a DMO1 dipolmeter (Wissenschaftlich-Technische Werkstätten) using the Guggenheim method[11]. The NMR spectra were recorded as shown in Table 1. Thin-layer chromatograms were made using 0.25 mm layers of silica gel GF–254 (E. Merck) on glass plates; spots were detected using a UV lamp.

TABLE 2

ANALYSES OF NEW COMPOUNDS

Compound[a]	M.p.(°C)	Purification[c]	Calculated (%)			Found (%)		
			C	H	S	C	H	S
$C_6F_4(SMe)_2$	89–90[b]	1, MeOH: 2	39.7	2.5	26.5	39.7	2.6	26.5
$C_6F_2(SMe)_4$	82–83	1, MeOH	40.2	4.0	43.0	40.1	4.0	43.1
$C_6F_4(SEt)_2$	46–47	1, MeOH	44.4	3.7	23.7	44.5	3.6	23.9
$C_6F_2(SEt)_4$	40–41	1, MeOH	47.4	5.7	36.2	47.6	5.7	36.1
$((MeS)_3C_6F_2)_2$	95–97	1, i-BuOH	43.0	3.6	38.3	43.3	3.7	38.7
$(EtSC_6F_4)_2$	59–60	1, i-BuOH	45.9	2.4	15.3	45.9	2.4	15.5
$(PhSC_6F_4)_2$	93–94	1, i-BuOH	56.0	2.0	12.5	56.0	2.6	12.5
$C_6Cl_2(SMe)_4$	145–146	1, MeOH	36.3	3.6	38.7	36.3	3.6	38.7

[a] All white solids.

[b] Lit.[8] 89–91°.

[c] 1 = recrystallization, 2 = sublimation.

The nucleophile (RS^-) was prepared by adding the thiol to an appropiate amount of sodium hydroxide in ethylene glycol. The perhaloaromatic compound was dissolved in pyridine, usually in air, and refluxed. The ratio of the volumes of ethylene glycol to pyridine was about 1:2. The nucleophile solution was added drop-wise through the condenser as rapidly as possible to the pyridine solution of the perhaloaromatic. The mixture was refluxed for 10 min, and then poured on to crushed ice and aq. HCl. The aqueous acid was extracted three times with ether, and the extract dried over $MgSO_4$. The ether was flashed off leaving the reaction products which were purified by distillation, recrystallization or sublimation. The crude product was examined by TLC and the purity of the purified products was checked by this method.

Various details of the reactant stoichiometry and major products isolated are shown in Table 3. Known products isolated were: C_6F_5SMe, b.p. 74–9°/22 mmHg, $n_D^{27.5}$ 1.4703 (lit.[2,12] b.p. 76°/22 mmHg, n_D 1.4703); $C_6F_4(SMe)_2$, m.p. 88.5–90° (lit.[8] 89–91°); C_6F_5SH, b.p. 140–4°, n_D^{25} 1.4632 (lit.[2] b.p. 143°, n_D^{20} 1.4629);

TABLE 3

Aromatic compound (mmoles)	Nucleophile (mmoles)	Major products	Yield[a] (%)
C_6F_6 (22.0)	MeS^- (22.0)	C_6F_5SMe	18
		$C_6F_4(SMe)_2$	16
C_6F_6 (76.0)	MeS^- (25.0)	C_6F_5SMe	36
		$C_6F_4(SMe)_2$	38
C_6F_6 (11.0)	MeS^- (60.0)	$C_6F_2(SMe)_4$	35
C_6F_6 (17.0)	HS^- (42.0)[b]	C_6F_5SH	3
		PFPPS[d]	
C_6F_6 (20.0)	EtS^- (10.0)	C_6F_5SEt	14
		$C_6F_4(SEt)_2$	14
C_6F_6 (20.0)	EtS^- (40.0)	$C_6F_4(SEt)_2$	61
C_6F_6 (10.0)	EtS^- (70.0)	$C_6F_2(SEt)_4$	40
C_6F_6 (20.0)	PhS^- (20.0)	$C_6F_4(SPh)_2$	28
C_6F_6 (20.0)	PhS^- (40.0)	$C_6F_4(SPh)_2$	47
C_6F_6 (20.0)	PhS^- (200.0)	see note c	
C_6F_6 (74.0)	$C_6F_5S^-$ (37.0)[b]	PFPPS[d]	
$C_6F_5{\bullet}C_6F_5$ (10.0)	MeS^- (20.0)	$MeSC_6F_4{\bullet}C_6F_4SMe$	44
$C_6F_5{\bullet}C_6F_5$ (10.0)	MeS^- (100.0)	$(MeS)_3C_6F_2{\bullet}C_6F_2(SMe)_3$	56
$C_6F_5{\bullet}C_6F_5$ (10.0)	EtS^- (20.0)	$EtSC_6F_4{\bullet}C_6F_4SEt$	76
$C_6F_5{\bullet}C_6F_5$ (10.0)	PhS^- (20.0)	$PhSC_6F_4{\bullet}C_6F_4SPh$	40
C_6Cl_6 (20.0)	MeS^- (20.0)	$C_6Cl_4(SMe)_2$	36
C_6Cl_6 (20.0)	MeS^- (80.0)	$C_6Cl_4(SMe)_2$	34
		$C_6Cl_2(SMe)_4$	35

[a] Yield as obtained after purification of the crude product, and based on the amount of the lesser reactant.

[b] Reaction studied under Ar.

[c] White product, empirical formula C_7H_7S, m.p. 70–1°.

[d] PFPPS = perfluoropoly(phenylene sulfide).

C_6F_5SEt, b.p. 78°/2 mmHg, n_D^{25} 1.4593 (lit.[5] b.p. 72°/2 mmHg, n_D^{23} 1.4648); $C_6F_4(SPh)_2$, m.p. 111–3° (lit.[3] 110–1°); $MeSC_6F_4 \cdot C_6F_4SMe$ m.p. 94–7° (lit.[10] m.p. 94–7°); $C_6Cl_4(SMe)_2$, m.p. 132–4° (lit.[4] m.p. 132–4°); perfluoropoly(phenylene sulfide), infrared spectra[13]. In the reaction of C_6F_6 + PhS^- it has been reported that $C_6F_4(SPh)_2$ and $C_6F_2(SPh)_4$ (m.p. 142–4°) are formed[3]. In the reactions described here it was not possible to isolate $C_6F_2(SPh)_4$, but when a large excess of the nucleophile was used an unknown product, m.p. 70.5–71.5°, of empirical formula C_7H_7S was isolated.

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REFERENCES

1 R. D. Chambers and D. J. Spring, *Tetrahedron, 27* (1971) 669.
2 P. Robson, M. Stacey, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1960) 4758.
3 P. Robson, T. A. Smith, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1963) 3692.
4 M. Kulka, *J. Org. Chem., 24* (1959) 237.
5 R. J. Neil and M. E. Peach, *J. Fluorine Chem., 1* (1971) 257.
6 J. C. A. Boeyens and F. H. Herbstein, *J. Phys. Chem., 69* (1965) 2153.
7 J. Burdon, *Tetrahedron, 21* (1965) 1101.
8 R. D. Chambers, J. A. Cunningham and D. A. Pyke, *Tetrahedron, 24* (1968) 2783.
9 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. 2, Pergamon, Oxford, 1966, p. 898.
10 K. Langille and M. E. Peach, *Canad. J. Chem., 48* (1970) 1474.
11 C. Smyth, *Dielectric Behaviour and Structure*, McGraw-Hill Inc., Toronto, 1955, p.225.
12 M. E. Peach and H. G. Spinney, *Canad. J. Chem., 49* (1971) 644.
13 M. E. Peach, *Canad. J. Chem., 46* (1968) 2699.