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SOME REACTIONS OF COPPER(I) PENTAFLUOROTHIOPHENOLATE AS A NUCLEOPHILE

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SUMMARY

Several aromatic compounds containing one or two C_6F_5S groups have been prepared by nucleophilic displacement reactions using $CuSC_6F_5$ in DMF solution. Aromatic iodine or bromine, rather than chlorine or fluorine is replaced by the SC_6F_5 group using $CuSC_6F_5$. A mechanism is postulated. New compounds prepared include p-$(C_6F_5S)_2C_6H_4$, o- and m-$(C_6F_5S)_2C_6F_4$ and p-$XC_6H_4SC_6F_5$(X=Cl, NO_2, I, CH_3, $CO_2C_2H_5$).

INTRODUCTION

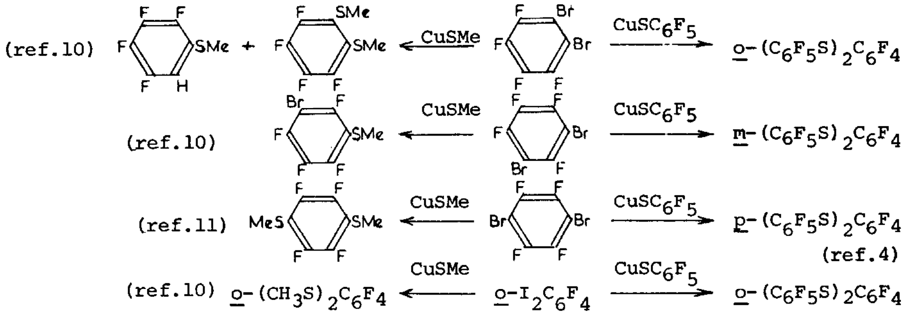
In previous studies the C_6F_5S group has been introducted into a variety of compounds using C_6F_5SH [1], C_6F_5SCl [2] and $(C_6F_5S)_2Pb$ [3]. In this paper some of the reactions of $CuSC_6F_5$ as a nucleophile have been examined.

One of the difficulties of using the pentafluorothiolate anion, $C_6F_5S^-$, as a nucleophile is its tendency to polymerize in basic solution. This has been counteracted by using the lead salt, $Pb(SC_6F_5)_2$, in reactions with highly reactive halides [3] and the copper(I) salt, $CuSC_6F_5$, in reactions with haloaromatics [4,5]. Both the lead and copper salts are readily prepared from pentafluorothiophenol [1].

The use of copper(I) thiolates for the introduction of thiolate groups into a variety of halogen containing compounds, by replacement of the halogen is now well established [6]. The halogen replaced is usually Br or I and not Cl or F, although activated Cl may be replaced [7]. Thus a selective halogen replacement can be achieved. Some reactions of $CuSC_6F_5$ with halogen contain aromatics have previously been reported, but all were compounds of the type BrC_6F_4X, $X=NO_2$, NH_2, Br, F where replacement of the bromine was observed [4,5]. These reactions have been extended to a variety of mono- and di-halogenated aromatic systems. The use of the analogous aliphatic compound copper(I) trifluoromethanethiolate has been well documented [8,9]. In all of these reactions DMF was used as the solvent.

RESULTS AND DISCUSSION

The reactions of the isomeric dibromotetrafluorobenzenes and o-diiodotetrafluorobenzene with the methanethiolate anion and copper(I) methanethiolate have been examined [10] and show that replacement of bromine, fluorine or protodebromination occurred.



In the reactions involvinng the copper(I) pentafluorothiophenolate only complete replacement of the bromine or iodine occurred.

The other reactions studied with $CuSC_6F_5$ are summarized below, the major product only being shown.

$$p\text{-Hal } C_6H_4X \xrightarrow{CuSC_6F_5} p\text{-}(C_6F_5S)C_6H_4X$$

Hal = I, X = Me, Cl, NO_2

Hal = Br, X = CO_2Et, OMe, $p\text{-}C_6H_4{\cdot}C_6H_5$

$$p\text{-}I_2C_6H_4 \xrightarrow{CuSC_6F_5} p\text{-}IC_6H_4SC_6F_5$$

$$p\text{-}(C_6F_5S)_2C_6H_4$$

Somewhat analogous reactions have been studied with $CuSCF_3$ [8,9]. The reaction has been extended to hexabromobenzene. Substitution of hexabromobenzene with the methanethiolate anion allowed replacement of 2 or 4 bromines with the methylthio group forming $p\text{-}Br_2C_6(SMe)_4$ and $p\text{-}(MeS)_2C_6Br_4$ [12].

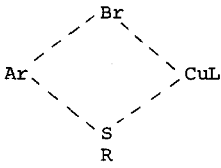
Protodebromination was also observed [12]. Hexabromobenzene or hexachlorobenzene were the starting material in the preparation of $C_6(SPh)_6$, using CuSPh as the source of the phenythio group [7]. The reaction of C_6Br_6 with $CuSC_6F_5$ was inconclusive as no single pure product could be isolated by the techniques used. This may be due to the relatively high molecular weight of the C_6Br_6 and any expected products, causing limited solubility etc. and subsequent difficulty in separation. Previously difficulty was encountered in the purification of products from the reactions of C_6Br_6 [12].

The copper (I) pentafluorthiophenolate obviously has properties as a nucleophilic source of the C_6F_5S group similar to that of other copper(I) thiolates. As it is readily prepared from the commercially available pentafluorothiophenol it can be considered an excellent reagent for introducing the pentafluorophenylthio group into aromatic compounds by replacement of an aromatic bromide or iodide and giving a relatively good yield of the desired product.

A detailed study of the reaction of CuSBu with C_6F_5Br has shown that the products are solvent dependent [13].

$$CuSBu + C_6F_5Br \rightarrow C_6F_5SBu + BuSC_6F_4H$$

In DMF, a weak ligand, exclusively bromine replacement occurred while in solutions containing thiourea protodebromination and exclusive fluorine replacement occurred. The mechanism of the reaction is not certain, but an intermediate such as



(I), L = solvent DMF

has been postulated for the bromine displacement, whereas an ionic complex $[CuL'_3]^+SR^-$ (L'=thiourea) can explain the fluorine displacement, fluorine being more readily displaced by the thiolate anion rather bromine. The formation of the intermediate I would also be applicable in the present study.

The new products isolated have been characterized by elemental analysis, infrared, mass, and proton NMR spectra. The infrared spectra indicated the presence of various functional groups but were not studied in detail.

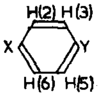
All the 70 eV mass spectra confirmed the molecular weights. In a previous study of the mass spectra of various elemental and aliphatic derivatives of pentafluorothiophenol, the $C_6F_5S^+$ ion (m/e 199) was always one of the most abundant ions [14]. In the present study the $C_6F_5S^+$ ion was only present in relatively small amounts in all the compounds studied, except *o*- and *m*-$(C_6F_5S)_2C_6F_4$ and *p*-$CH_3C_6H_4(SC_6F_5)$. Obviously some different fragmentation is occurring when the C_6F_5S group is bound to a hydrogen containing aromatic nucleus, and the C_6F_5S group is not being fragmented as an ion. Comparison of the primary ion spectra of *o*- and *m*-$(C_6F_5S)_2C_6F_4$ showed that these were virtually identical and that the mass spectra cannot be used to distinguish readily between these two isomers. Similar observations have shown that it was not possible to distinguish between the isomers of $C_6F_3H(NH_2)(SMe)$ using primary ion mass spectra or ion kinetic energy spectra [15]. Simple initial fragmentation modes could be deduced from the primary ion spectra, but more detailed fragmentation schemes were not investigated.

The proton NMR spectra of all the compounds have been examined. The fluorine NMR spectra would give little information on the structures of the compounds as the C_6F_5S group is present in every compound and in the isomers of $(C_6F_5S)_2C_6F_4$ the fluorine signals from the C_6F_4 group would probably overlap those of the C_6F_5, making the spectrum extremely complicated. Details of the proton NMR spectra are shown in Table 1 together with coupling constants.

TABLE 1

Summary of proton N.M.R. data

Compound	Chemical shift/p.p.m.	Coupling Constants/Hz			
		J(2,3)	J(2,5)	J(2,6)	J(3,5)
p-$(C_6F_5S)_2C_6H_4$	7.25S (ArH)				
p-$IC_6H_4SC_6F_5$	7.06D'	8.2	0.4	2.4	1.8
	7.61D'				
p-$O_2NC_6H_4SC_6F_5$	7.15D'	8.7	0.3	3.6	2.5
	7.32D'				
p-$ClC_6H_4SC_6F_5$	7.31S (ArH)				
p-$C_2H_5CO_2C_6H_4SC_6F_5$	1.29T (CH_3)	8.0	0.5	2.3	1.5
	4.38Q (CH_2)				
	7.26D'				
	7.97D'				
p-$CH_3OC_6H_4SC_6F_5$	3.81S (CH_3)	7.7	0	0.6	1.0
p-$C_6H_5C_6H_4SC_6F_5$	7.49M (ArH)				



S: singlet D': doublet (splitting) Q: quartet

T: triplet Q': quartet (splitting) M: multiplet

In the compounds p-$(C_6F_5S)_2C_6H_4$ and p-$ClC_6H_4(SC_6F_5)$ only a single signal was observed. In p-$ClC_6H_4(SC_6F_5)$ the electronegativity of the SC_6F_5 group must be almost identical with that of chlorine. In the para disubstituted compounds $XC_6H_4(SC_6F_5)$ an AA'BB' spectrum was observed. The coupling constants were deduced and checked by using a computer simulated spectrum. Due to the similarities of the chemical shifts it was not possible to uniquely assign either the chemical shifts or coupling constants.

EXPERIMENTAL

All the reagents were available commercially, except $CuSC_6F_5$ which was readily prepared from C_6F_5SH and $CuSO_4$ [1]. Microanalyses were performed by Mikroanalytisches Laboratories, Beller, Göttingen, W. Germany. The analytical data and physical properties of the new compounds are shown in Table 2.

TABLE 2

Chemical analyses and physical properties of compounds isolated

Compound	+ M.p./°C	Calculated (%)			Found (%)		
		C	H	S	C	H	S
o-$(C_6F_5S)_2C_6F_4$	124-5	39.6	-	11.7	39.6	-	11.8
m-$(C_6F_5S)_2C_6F_4$	123-4	39.6	-	11.7	39.5	-	11.9
p-$(C_6F_5S)_2C_6H_4$	152-3	45.9	0.92	13.6	45.6	0.85	13.5
p-$IC_6H_4SC_6F_5$	91-2	35.8	1.00	8.0	36.1	1.11	8.1
p-$O_2NC_6H_4SC_6F_5$	80-1	44.9	1.26	-	45.1	1.09	-
p-$ClC_6H_4SC_6F_5$	45-6	46.4	1.30	10.3	46.8	1.11	10.5
p-$EtCO_2C_6H_4SC_6F_5$	70-1	51.7	2.60	9.2	51.9	2.63	9.3
p-$MeOC_6H_4SC_6F_5$*	31-3	51.0	2.30	10.5	51.1	2.07	10.9
p-$MeC_6H_4SC_6F_5$	35-6	53.8	2.43	11.1	54.4	2.29	11.1
p-$C_6H_5C_6H_4SC_6F_5$	112-3	61.4	2.57	9.1	61.1	2.87	9.2

* Lit. b.p. 94-5°/0.15 Torr [2]

+ all white

Mass spectra (70 eV) were recorded on a DuPont/C.E.C. Model 21-491 mass spectrometer using direct introduction techniques. NMR spectra were recorded in $CDCl_3$ solution using TMS as an internal standard on a Varian HA 100. Infrared spectra were recorded on a Perkin Elmer Model 457 spectrophotometer as thin films, as mulls with Nujol or hexachlorobutadiene, or as KBr discs.

All reactions were studied by the same general technique. A solution of the requisite organohalogen starting material (20 mmoles) in DMF (75 mL) was heated at 140°C for 15 mins. A 50% excess of $CuSC_6F_5$ was added and the mixture refluxed, with stirring, for 2 h. The reaction was quenched by pouring onto ice (500 g)/HCl (250 mL). The solution was extracted twice with 200 mL ether. After drying the crude product was isolated by removal of the ether. The number of compounds in the crude product was determined by TLC. The major products were purified by recrystallization, column chromatography, or vacuum distillation. Details of the specific reactions are listed in Table 3.

TABLE 3

Reaction products and purification

Substrate	Major product	Minor Products	Yield (%)	Purification*
o-$Br_2C_6F_4$	*o*-$(C_6F_5S)_2C_6F_4$	2	61	1, 3A
o-$I_2C_6F_4$	*o*-$(C_6F_5S)_2C_6F_4$	6	64	1, 3A
m-$Br_2C_6F_4$	*m*-$(C_6F_5S)_2C_6F_4$	3	61	1, 3A
p-$I_2C_6H_4$	*p*-$(C_6F_5S)_2C_6H_4$	4	59	1, 3A
	p-$(C_6F_5S)C_6H_4I$		22	1, 3A
p-$IC_6H_4NO_2$	*p*-$(C_6F_5S)C_6H_4NO_2$	3	65	1, 3B
p-IC_6H_4Cl	*p*-$(C_6F_5S)C_6H_4Cl$	2	54	1, 3A
p-$BrC_6H_4CO_2C_2H_5$	*p*-$(C_6F_5S)C_6H_4CO_2C_2H_5$	2	58	1, 3B
p-$BrC_6H_4OCH_3$	*p*-$(C_6F_5S)C_6H_4OCH_3$	1	60	2, 3A
p-$IC_6H_4CH_3$	*p*-$(C_6F_5S)C_6H_4CH_3$	2	52	2, 3A
p-$C_6H_5C_6H_4Br$	*p*-$(C_6F_5S)C_6H_4C_6H_5$	2	67	1, 3A

* 1 - recrystallization (ethanol) } initial purification
2 - vacuum distillation }
3 - column chromatography: A - hexane B - carbon tetrachloride

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