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THE THIOLATE ANION AS A NUCLEOPHILE
PART XII*. REACTIONS OF LEAD(II) BENZENETHIOLATE

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SUMMARY

The reactions of various fluoroaromatics, $C_6F_{6-x}H_x$, and C_6F_5X (X = C_6F_6, Cl, Me, NO_2, CF_3, COCl, CH_2Br, OMe, and NH_2) with lead(II) benzenethiolate in DMF have been examined. Lead thiolate acted as an excellent source of benzenethiolate anions and displacement of fluorine, chlorine or the nitro group was observed. The new products have been characterized by elemental analysis, and NMR (H-1 and F-19), infrared and mass spectroscopy.

INTRODUCTION

There are many variables that can affect the nuclephilic displacement reaction of fluorine in fluoroaromatics with the thiolate anion.

$$C_6H_{6-x}F_x + ySR^- \longrightarrow C_6H_{6-x}F_{x-y}(SR)_y + yF^-$$

Such variables as the reactant stoichiometry, the reaction solvent, the bulk of the thiolate anion and the nature of the fluoroaromatic have been partially studied previously [1,2,3,4]. In all previous studies in the series the thiolates were used as their sodium salts. This paper describes the reactions of lead(II) benzenethiolate with various fluoroaromatics in N,N-dimethylformamide (DMF) as solvent.

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*For Part XI, see ref. 1

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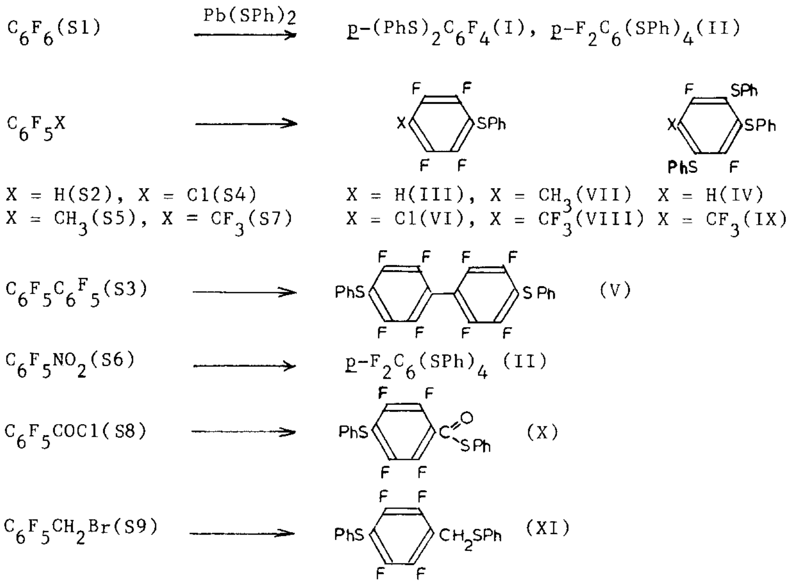
The reactions of thiolate anions with various haloaromatics have been described. The reaction involved mainly displacement of fluoride or chlorid ion by metal thiolates. The metal thiolates used were almost exclusively the alkali metal thiolates in various solvents. Some examples include LiSR in DMF [5]; NaSR in ethylene glycol/pyridine [1], in DMF [2], in HMPA [2,6]; KSR in ethylene glycol/pyridine [7] or DMF [8].

Reactions of copper(I) thiolates with bromofluoroaromatics have demonstrated that in some circumstances exclusive replacement of the bromine will occur, but under different conditions exclusive displacement of fluorine can also occur [9,10,11]. Exclusive displacement of the fluorine with CuSR in C_6F_5Br only occurred when thiourea was added as a coordinating ligand for the copper ions [9]. There are a large number of other metal thiolates known and this paper described some reactions of lead(II) benzenethiolate with various fluoroaromatics.

RESULTS AND DISCUSSIONS

The reactions of lead(II) benzenethiolate with various fluoroaromatics have been studied and the results are shown schematically below. Only the major products were isolated.



Lead(II) benzenthiolate is readily prepared and can be stored at room temperature in the atmosphere [12,13]. The yellow colour of the thiolate acts as an indicator of the completion of the reaction, as the colourless fluoride is formed.

$$Pb(SPh)_2 + C_6F_6 \longrightarrow PbF_2 + \underline{p}\text{-}(PhS)_2C_6F_4$$

This convenience is not available when the colourless alkali metal thiolates are used.

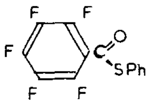
Although the reactions of various sodium thiolates Na^+SR^- (R = Me, Et, i-Pr, t-Bu) have been examined, there are only scant reports of the reactions of sodium or potassium benzenethiolates with fluoroaromatics, these being restricted to hexafluorobenzene [7,14], decafluorobiphenyl [14], pentafluorobenzene [15] and p-bis(methylthio)tetrafluorobenzene [16]. The same products were obtained from lead(II) benzene thiolate and hexafluorobenzene, decafluorobiphenyl and pentafluorobenzene. The series of fluoroaromatics has been extended to the tetrafluorobenzenes and a variety of compounds of the type C_6F_5X. The group X could be activating for nucleophilic substitution, eg. X = COSPh, NO_2 or deactivating eg. X = NH_2, OMe, when compared with hexafluorobenzene (X = F). No products could be isolated from the reactions with the tetrafluorobenzenes (<u>ortho</u>, <u>meta</u> and <u>para</u>), pentafluoroaniline or pentafluoroanisole, although products were obtained in their reactions with sodium methanethiolate in ethylene glycol/pyridine as solvent [16,4,21].

Studies of the reactions of the nitrofluorobenzenes with sodium methanethiolate in ethylene glycol/pyridine mixture showed displacement of some or all of the aromatic fluorine, but not the nitro group [3]. In some circumstances the nitro group may be a leaving group, as in the reaction of lithium methanethiolate with chloronitrobenzenes in DMF [5]. The formation of $\underline{p}\text{-}F_2C_6(SPh)_4$ from pentafluoronitrobenzene may therefore be an effect of the solvent. The reactions of fluoronitrobenzenes with sodium methanethiolate have not been studied in DMF, but lithium methanethiolate reacts with chloronitrobenzenes to give replacement of chlorine in methanol and then replacement of the nitro group in DMF [5]. In the case of chloropentafluorobenzene the major product was obtained by fluorine replacement, rather than replacement of chlorine.

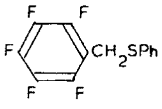
The reactant stoichiometry was varied, so that partial replacement of the aromatic fluorine could be observed, as well as possible complete displacement. A comparison of the reaction of lead(II) benzenethiolate and sodium methanethiolate, both in DMF, with the simple fluoroaromatics $C_6F_{6-x}H_x$ shows that while total replacement of fluorine can occur with the sodium thiolate, some fluorines remain on the ring using the lead(II) thiolate. This may be a solvent effect, but could also be caused by the formation of a weak complex between the lead(II) ion and the product. Complexes of some (methythio)fluorobenzenes, $C_6H_xF_y(SMe)_z$ with metal ions have been reported [17]. The formation of a complex, even a weak complex, could inhibit further reaction of the ligand with the lead(II) thiolate. The solvent, DMF, is also known to be a relatively good donor solvent [18] and may coordinate any Pb^{2+} ions [19]. The difference in reactivities is probably not due to the relative sizes of the methyl and phenyl groups as hexakis-(phenylthio)benzene, $C_6(SPh)_6$, has been prepared from hexachlorobenzenes and copper(I) benzenethiolate [20]. However, it has been noted previously that the relatively bulky anion $(CH_3)_3CS^-$ cannot substitute all the fluorines in fluorobenzenes whereas complete substitution occurred with CH_3S^- under the same conditions [1].

While the mechansim of the reaction has not been studied, it can be postulated that lead benzenethiolate at least partially ionizes in the DMF forming the benzenethiolate anion, PhS^-, which reacts with the fluoroaromatic. A similar mechanism has been proposed for the reaction of copper(I) thiolates with fluoroaromatics in the presence of thiourea, when fluorine displacement was observed [9].

The system was extended to hexachlorobenzene, but no pure single product could be isolated from these reactions. Obviously the displacement of an aromatic fluorine is cleaner than the corresponding chlorine when using lead(II) thiolates. Displacement of aliphatic chloride or bromide is, however, easy and the intermediates XII and XIII must be formed from S8 and S9.



XII



IIIX

The identity of the new products was confirmed by chemical analysis and mass spectroscopy (for molecular weight). The presence of the various functional groups was shown by infrared spectroscopy. The structure was deduced from the NMR spectra (H-1 and F-19) as described in previous parts [1]. Details of the proton and fluorine NMR spectra are tabulated in Table 1.

The structures of some of the products were deduced by comparison with the structures of the methylthio analogs [16,21]. Although in some cases coupling constants of the compounds $PhSC_6F_4X$ could not be deduced, the two distinct fluorine resonances of equal intensity clearly indicated a *para* structure. In the compounds C_6F_5X, when X = CH_3 or CF_3 coupling of the H or F to the *ortho* and *para* fluorine is observed J(CF_3-F *ortho*) 22.5; J(CF_3-F *para*) 1.4; J(CH_3-F *ortho*) 2.3; J(CH_3-F *para*) 1.4Hz.) [22]. Similar couplings are also observed in the products VII, VIII and IX although the coupling to the *para* fluorine may not be resolved. The large increase in the coupling constant in IX, where there is now a PhS group, as well as a F, *ortho* to the CF_3, supports the hypothesis that this is a through space effect, partially determined by the bulk of the *ortho* substituents.

The experimental technique was varied somewhat from previous reactions [1]. The reaction was quenched by pouring onto ice water and the product extracted with hexane. When sodium thiolates were used the reaction was quenched by pouring onto ice/HCl. The elimination of the HCl in the quenching also prevents the formation of any free thiol at this stage.

As an extension of this work some reactions of tin(II) benzenethiolate and mercury(II) benzenethiolate have been examined. The mercury(II) thiolate decomposed within one hour in the warm DMF to form mercury and diphenyldisulfide and was, therefore, useless. However preliminary studies indicate that tin(II) benzenethiolate reacts in the same way as lead(II) benzenethiolate

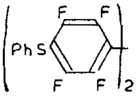
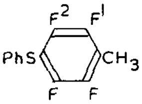
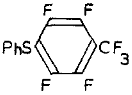
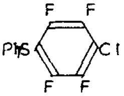
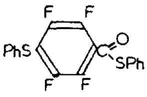
It has been shown that lead(II) thiolates, in this case lead(II) benzenethiolate is an excellent reagent for nucleophilic displacement of fluorine in various fluoroaromatics. Problems encountered with the smell of the thiols can be reduced as the lead(II) thiolate can be prepared and stored, whereas the sodium thiolates were always prepared in situ, additionally the elimination of HCl in the quenching stage prevents formation of the thiol.

EXPERIMENTAL

All reagents were available commercially. $Pb(SPh)_2$ was prepared by a known technique [12,13]. Microanalyses were performed by Canadian Microanalytical Services Ltd., Vancouver, B.C.. The analytical data and physical properties of the new compounds are shown in Table 2. The mass spectra (70eV) were recorded on a DuPont Model 21-451 Mass Spectrometer, using a direct introduction technique. Infrared spectra were recorded on a Perkin Elmer Model 683 Infrared Spectrometer between CsBr plates or an KBr discs.

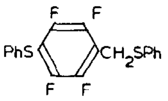
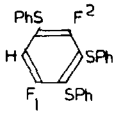
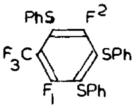
TABLE 1

Summary of NMR data

Compound		Chemical shift p.p.m.			Coupling constants/Hz
	(V)	H	7.38	M	
		F	130.0	DDD	J(F-F *ortho*) 18.8
					J(F-F *meta*) 1.4
		F	135.3	DDD	J(F-F para) 7.5
	(VII)	H(Me)	2.27	T	J(Me-F ortho) 2.1
		H(Ar)	7.23	M	
		F-1	150.6	DDT	J(F *ortho* - Me) 2.1
					J(F-F *ortho*) 23.6
		F-2	142.5	DD	J(F-F *meta*) <1.0
					J(F-F *para*) 12.7
	(VIII)	H(Ar)	7.38	M	
		F(CF_3)	54.0	T	J(CF_3-F *ortho*) 22.1
		F	138.2	M	
		F	129.2	M	
	(VI)	H	7.39	M	
		F	137.8	M	
		F	129.6	M	
	(X)	H	7.32	M	
		H	7.49	M	
		F	138.1	DDD	J(F-F *ortho*) 24.0
					J(F-F *meta*) 1.4
		F	129.1	DDD	J(F-F *para*) 13.1

(Continued)

TABLE 1 (cont.)

Compound	Chemical shift p.p.m.			Coupling constants/Hz
 (XI)	$H(CH_2)$	4.04	T	J(H-F *ortho*) 1.20
	H(Ar)	7.25	M	
	F	140.3	M	
	F	131.3	M	
 (IV)	H	6.55	DD	J(H-F2)6.2; J(H-F1)8.6
	F-1	101.8	DD	J(F-H) 8.7; J(F-F2)15.2
	F-2	99.7	DD	J(F-H) 6.4; J(F-F1)14.9
 (IX)	H(Ar)	7.14	M	
	H(Ar)	7.20	M	
	H(Ar)	7.24	M	
	$F(CF_3)$	51.3	DD	J(CF_3-F1)35.3; J(CF_3-F2)<1.0
	F-1	100.8	QD	J(F-CF_3)34.8; J(F-F2)16.9
	F-2	87.2	QD	J(F-CF_3)1.8; J(F-F1)16.9

All spectra recorded in $CDCl_3$ solution with TMS or CF_3CO_2H as internal or external standard. Fluorine corrected to $CFCl_3$ as internal standard.

D = doublet, T = triplet, Q = Quartet, M = multiplet

The NMR Spectra of $CDCl_3$ solutions were recorded on a Varian EM360L NMR Spectrometer using TMS (H-1) and F_3CCO_2H (F-19) as internal and external standards respectively.

The reaction procedure was similar to that employed previously for CuSPh [23]. The fluoroaromatic (10 mmol) was dissolved in 75 mL of DMF and a stoichiometric amount of $Pb(SPh)_2$ added. The mixture was refluxed and stirred until the yellow colour had disappeared, or for a maximum of one week. The reaction mixture was filtered while hot, and the filtrate poured onto 250 mL ice/water. The mixture was extracted with three 75 mL portions of hexane, which were dried over $MgSO_4$. The crude product was obtained after removal of the solvent at low pressure and purified. Details of the reactant stiochiometry and purification procedures are shown in Table 3. No attempt was made to isolate the minor products.

TABLE 2

Physical properties and chemical analyses of new compounds

	m.p./°C	Calculated(%)		Found(%)	
Compound	b.p./°C/Torr	C	H	C	H
VI	24/0.9 39.5-41.5	49.2	1.70	49.6	1.55
VII	71/0.015	57.4	2.96	57.3	3.04
VIII	105/0.05	47.8	1.50	47.8	1.29
IX	75-77	59.3	2.99	59.2	2.90
X	66-68	57.8	2.60	57.5	2.19
XI	87-89	60.0	3.20	59.8	2.93

TABLE 3

Reaction parameters

Starting compound	Product	Reactant Ratio $Pb(SPh)_2$:ArF	Time* (hrs.)	Yield† (%)	Purification
S1	I	1:1	3	75	1 MeOH
S1	II	2:1	24	10	1 MeOH
S1	II	3:1	192i	3	1 MeOH
S2	III	1:2	20	95	2
S2	IV	3:2	194i	5	1 MeOH
S3	V	1:1	5	88	1 MeOH
S7	IX	3:1	213i	35	1 MeOH
S4	VI	1:2	2	99	1 MeOH
S5	VII	1:2	112	67	2
S6	II	2:1	200	7	1 MeOH
S7	VIII	1:2	18**	55	2
S7	IX	3:2	211	34	1 MeOH
S8	X	1:1	18	46	1 MeOH
S9	XI	1:1	23	99	1 MeOH

*Color change showed reaction complete, except where i = incomplete

1 = recrystallization;

2 = vacuum distillation

**No heat

†Based on fluoroaromatic

Known products were characterized by their m.p.s. or b.p.s. or NMR spectra: I, m.p. 108-111° (lit.[7]110-111°), NMR [14]; II, m.p. 136; (lit.[7]142-144°), NMR [15]; III, b.p. 105.5°/1.8mm (lit.[16]62-4°/0.4mm), NMR [16]; IV, m.p. 93-4° (lit. [16]92-3°) NMR [16]; V, m.p. 95-6° (lit. [14]93-4°).

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