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THE THIOLATE ANION AS A NUCLEOPHILE
PART XIV*. FURTHER REACTIONS OF TIN(II) ARENETHIOLATES

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SUMMARY

The reactions of tin(II) benzenethiolate in DMF with hexafluorobenzene, chloropentafluorobenzene and bromopentafluorobenzene have been compared. Replacement of fluorine and chlorine by the phenylthio group and protodebromination were observed. DMF was a better solvent than either ethylene glycol/pyridine mixture (1:2) or diglyme for the reaction. New products have been isolated and characterized from the reactions of tin(II) p-chlorobenzenethiolate with hexafluorobenzene, decafluorobiphenyl, octafluorotoluene and pentafluorobenzyl bromide.

INTRODUCTION

Tin(II) arenethiolates are readily prepared from tin(II) acetate and an arenethiol [1,2] and can be used for the introduction of an arylthio group into fluoro and chloro-aromatics [1,3,4]. The thiols studied have included benzenethiol, p-toluenethiol, p-fluorobenzenethiol and 1,2,4,5-tetrafluorobenzenethiol. This paper extends this series to include p-chlorobenzenethiol. Previously the reactions of tin(II) arenethiolates have been studied in DMF, and the effect of changing the solvent to ethylene glycol/pyridine mixture or diglyme has been studied. A mixture of 1:2 ethylene glycol/pyridine has been employed as the solvent in some reactions of sodium alkane and arenethiolates with fluoroaromatics [5]. The rate of reaction, as evidenced by the enhanced product yield, was increased in the presence of sodium fluoride. Fluoride ion acts as a catalyst in the reaction of pentafluorophenyl derivatives with nitrogen nucleophiles [6].

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* For Part XIII, see [1].

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RESULTS AND DISCUSSION

The effect of varying the solvent has been examined by studying the reactions of hexafluorobenzene in DMF, ethylene glycol/pyridine (1:2) and diglyme.

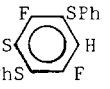
$$Sn(SR)_2 + C_6F_6 \longrightarrow \underline{p}\text{-}(RS)_2C_6F_4 \quad (\underline{1})$$
$$R = C_6H_5(\underline{a}),\ \underline{p}\text{-}ClC_6H_4(\underline{b})$$

Details of these reactions and product yields are shown in Table 1. Comparison of the reactions within the groups R = C_6H_5 (reactions 1,2,3,4) and $\underline{p}$-ClC_6H_4 (reactions 5,6) shows that DMF is the best solvent and diglyme the worst. The solvent dependency of the reactions of sodium methanethiolate with fluoroaromatics showed that while only partial fluorine substitution occurred in ethylene glycol/pyridine, complete replacement occurred in DMF [5,7]. Comparison of reactions 1 and 5 or 2 and 6 show that tin(II) benzenethiolate is a better reagent in these reactions than tin(II) $\underline{p}$-chlorobenzenethiolate. This would be anticipated if the reactions involved formation of the free thiolate anion.

Potassium fluoride shows catalytic activity in the substitution reactions of haloalkanes with benzenethiol [8] and the pentafluorophenyl group with nitrogen nucleophiles [6]. This has been attributed to hydrogen bonding between the nucleophile and the fluoride ion. The reactions of tin(II) benzenethiolate with hexafluorobenzene, chloropentafluorobenzene and bromopentafluorobenzene in DMF have been studied with and without added sodium fluoride.

$$C_6F_6 + Sn(SPh)_2 \longrightarrow \underline{p}\text{-}(PhS)_2C_6F_4\ (\underline{1a}),\ \underline{p}\text{-}F_2C_6(SPh)_4\ (\underline{2})$$

$$C_6F_5Cl + Sn(SPh)_2 \xrightarrow{NaF} \underline{p}\text{-}F_2C_6(SPh)_4\ (\underline{2})$$

$C_6F_5Br + Sn(SPh)_2 \xrightarrow{NaF}$  (3)

In the absence of the fluoride ion in the reactions with chloropentafluorobenzene and bromopentafluorobenzene oxidation of the tin(II) benzenethiolate was observed, forming the disulfide, $(PhS)_2$.These reactions are listed in Table 1 as 1,7,8 (C_6F_6 + $Sn(SPh)_2$) 9,10 (C_6F_6 + $2Sn(SPh)_2$) 11,12 (C_6F_5Cl + $Sn(SPh)_2$) and 13,14 (C_6F_5Br + $Sn(SPh)_2$). The formation of $\underline{1a}$, $\underline{p}$-$(PhS)_2C_6F_4$, appears to be rapid, whether or not the fluoride ion is present; however a colour change was observed after 15 minutes in the catalysed reaction, while

TABLE 1

Reaction conditions, products and yields

Reaction Number	$Sn(SR)_2$ R =	ArF	$Sn(SR)_2$:ArF (mmol)	Solvent*	NaF (mmol)	Time	Product	Yield (%)
1	Ph	C_6F_6	10:10	DMF	0	2h	1a	68
2	Ph	C_6F_6	10:10	EG/Py	0	17.5h	1a	33
3	Ph	C_6F_6	10:10	EG/Py	0	6h	1a	11
4	Ph	C_6F_6	10:10	DIG	0	18h	1a	1
5	ClC_6H_4	C_6F_6	10:10	DMF	0	3h	1b	22
6	ClC_6H_4	C_6F_6	10:10	EG/Py	0	17.5h	1b	3
7	Ph	C_6F_6	10:10	DMF	30	0.25h	1a	70
8	Ph	C_6F_6	10:10	DMF	90	2h	1a	68
9	Ph	C_6F_6	10:5	DMF	30	3.75h	2	54
10	Ph	C_6F_6	10:5	DMF	0	3.75h	2	29
11	Ph	C_6F_5Cl	10:5	DMF	30	16h	2	7
12	Ph	C_6F_5Cl	20:10	DMF	0	16.4h	$(PhS)_2$	19
13	Ph	C_6F_5Br	10:10	DMF	30	0.4h	3	13
14	Ph	C_6F_5Br	10:10	DMF	0	0.4h	$(PhS)_2$	5
15	ClC_6H_4	$C_6F_5C_6F_5$	10:10	DMF	0	3h	4	70
16	ClC_6H_4	$C_6F_5CF_3$	10:10	DMF	0	3h	5	7
17	ClC_6H_4	$C_6F_5CH_2Br$	10:10	DMF	0	3h	6	10

* EG/Py = ethylene glycol/pyridine ratio 1:2, DIG = diglyme

this only occurred after 2 hours in the non catalysed reaction. The catalytic effect of the fluoride ion is shown in the formation of 2 from hexafluorobenzene and chloropentafluorobenzene. The initial reaction of chloropentafluorobenzene with tin(II) arenethiolates produced p-RSC_6F_4Cl [1] which must be further substituted by replacement of the chlorine and two fluorines to form 2. In the substitution reactions of bromopentafluorobenzene with sodium methanethiolate in ethylene glycol/pyridine protodebromination was observed and the analog of 3 (with the phenyl replaced by methyl) could be isolated [9]. Substitution of the bromine occurred when bromopentafluorobenzene was treated with copper(I) benzenethiolate forming phenyl(pentafluorophenyl)sulfide, $C_6H_5SC_6F_5$ [10].

The reactions of tin(II) p-chlorobenzenethiolate with various fluoroaromatics have been examined (R = p-ClC_6H_4).

$$Sn(SR)_2 + C_6F_6 \longrightarrow \underline{p}\text{-}(RS)_2C_6F_4 \quad (\underline{1b})$$

$$Sn(SR)_2 + C_6F_5C_6F_5 \longrightarrow (\underline{p}\text{-}RSC_6F_4)_2 \quad (\underline{4})$$

$$Sn(SR)_2 + C_6F_5CF_3 \longrightarrow RS\text{-}C_6F_2(SR)\text{-}CF_3 \quad (\underline{5})$$

$$Sn(SR)_2 + C_6F_5CH_2Br \longrightarrow RS\text{-}C_6F_2\text{-}CH_2SR \quad (\underline{6})$$

The formation of $\underline{p}$-$CF_3C_6F_4SR$ and $C_6F_5CH_2SR$, both observed in the reactions of $Sn(STol\text{-}\underline{p})_2$ with $C_6F_5CF_3$ and $C_6F_5CH_2Br$ [1] must be intermediates in the formation of 5 and 6. Similarly the monosubstituted product C_6F_5SR must be an intermediate in the formation of 1b. Under similar reaction conditions, 3h reaction time, pentafluorobenzene did not react, although it has been observed to react with $Sn(SPh)_2$ [1].

The new compounds 1b, 4, 5 and 6 have been characterized by elemental analysis. The structures have been assigned on the basis of the F-19 NMR spectra by comparison with the analogs when R = Ph and $\underline{p}$-Tol [1]. In the C-13 NMR spectra, signals corresponding to the $\underline{p}$-ClC_6H_4S group can be assigned by comparison with the reported spectrum of the thiol [11]. Due to multiple C-C_x-F coupling (x= 0, 1, 2) on the fluoroaromatic ring and the presence of three non-equivalent $\underline{p}$-ClC_6H_4S groups, assignment of the C-13 signals in 5 was impossible. Details of the C-13 NMR spectra are shown in Table 2.

Comparison of the reactions of tin(II) [1], lead(II) [12] and nickel(II) [13] arenethiolates with fluoroaromatics in DMF show that the reactivity is generally comparable, giving partial replacement of the aromatic fluorines. Rigorous comparison is not possible due to the differing reaction conditions. However sodium thiolates when used in DMF can produce complete replacement of the fluorines in fluoroaromatics [7]. In contrast silver(I) and copper(I) arenethiolates in DMF will not replace fluorine in fluoroaromatics, but will substitute bromine in bromofluoroaromatics [14, 10].

EXPERIMENTAL

Tin(II) arenethiolates were prepared from tin(II) acetate and the corresponding arenethiol [2]. The various fluoroaromatics and thiols were available commercially. NMR spectra were recorded as $CDCl_3$ solutions on a Varian EM 360L NMR spectrometer (H-1 and F-19) using TMS and $CFCl_3$ as internal standards and on a Nicolet 360NB (C-13) NMR spectrometer (TMS as

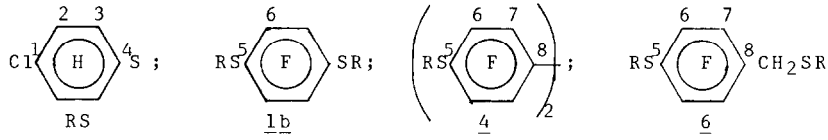
TABLE 2

Carbon-13 NMR

Chemical shifts (ppm., relative to TMS as internal standard)						
Compound	C-1	C-2	C-3	C-4	C-5,C-8	C-6,C-7
RSH	131.6S	129.0S	130.6S	129.3S		
RSH*	131.6	130.0	130.9	128.9		
1b	134,5S	129.5S	132.5S	131.1S	130.6S	146.7DDD
4	134.8S	129.6S	132.6S	130.2S	107.5T,116.8T	143.6DD,146.6DD
6	134.5S 131.7S	129.5S 129.4S	132.5S 131.9S	131.1S 131.4S	130.6S,130.7S	146.6DD

Coupling constants (Hz)		
Compound	Origin	
1b	C-6,7	J(C-F) 254.6; J(C-C-F) 19.6; J(C-C-C-F) 4.7
4	C-6,7	J(C-F) 256.4; J(C-C-F) 16.2, 19.9
6	C-6,7	J(C-F) 250.2; J(C-C-F) 21.9

* see ref. 11.



internal standard). Elemental analyses were performed by Canadian Microanalytical Services Ltd., New Westminster, British Columbia.

In a generalized reaction procedure, 10 mmoles of the tin(II) thiolate in 30 mL DMF was added to a solution of 10 mmoles of the fluoroaromatic in 70 mL refluxing DMF and the mixture refluxed for 3h. The colour changed from a darkish brown to a lighter one. The hot reaction mixture was filtered and poured onto ice. The solid suspension of the product was filtered off and extracted with Et_2O, C_6H_{14} or $HCCl_3$. The extracts were dried with $MgSO_4$ and after removal of the solvent, the products were purified by recrystallization. Product purity was confirmed by TLC. A similar procedure was used for the reactions with 1:2 ethylene glycol/pyridine mixture or diglyme as solvent.

Known compounds were identified by comparison of the m.p. with literature values: 1a, m.p. 109.5-111.0°, lit. m.p. 110-111° [15]; 2, m.p. 137-139°, lit. m.p. 142-144° [15]; 3, m.p. 90-92°, lit. m.p. 92-93° [16]; $(PhS)_2$, m.p. 60-62°, lit. m.p. 61-62°.

The new compounds isolated were characterized.

1b, white, m.p. 168-170°. Analysis: Found:C, 49.6; H, 1.88%. $C_{18}H_8Cl_2F_4S_2$ requires C, 49.6; H, 1.85%. H-1 NMR: 7.22M ppm.; $J(H_{ortho})$ 7.4 Hz. F-19 NMR: 133.3S ppm.

4, white, m.p. 129-131°. Analysis: Found: C, 49.5; H, 1.46%. $C_{24}H_8Cl_2F_8S_2$ requires C, 49.4; H, 1.38%. H-1 NMR: 7.33M ppm.; $J(H\text{-}H_{ortho})$ 6.6 Hz. F-19 NMR: 133.5D (F-6), 138.4DD (F-7) ppm.; $J(F\text{-}F_{ortho})$ 25.6 $J(F\text{-}F_{meta})$ 3.8, $J(F\text{-}F_{para})$ 13.2 Hz.

5, white, m.p. 109-111°. Analysis: Found: C, 49.2; H, 2.15%. $C_{25}H_{12}Cl_3F_5S_3$ requires C, 49.2; H, 1.98%. F-19 NMR: 59.6D (CF_3), 88.8D (F-6) 102.3M (F-7) ppm.; $J(CF_3\text{-}F_{ortho})$ 35.7, $J(F\text{-}F_{para})$ 18.8 Hz.

6, white, m.p. 70-73°. Analysis: Found: C, 50.7; H, 2.26%. $C_{19}H_{10}Cl_2F_4S_2$ requires C, 50.8; H, 2.24%. H-1 NMR: 1.45S (CH_2), 7.24M (ArH) ppm.; $J(H\text{-}H_{ortho})$ 6.6 Hz. F-19 NMR: 133.9M (F-6), 142.5M (F-7) ppm.; $J(F\text{-}F_{ortho})$ 22.6, $J(F\text{-}F_{meta})$ 5.6, $J(F\text{-}F_{para})$ 12.0 Hz.

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