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THE THIOLATE ANION AS A NUCLEOPHILE

PART XIII*. REACTIONS OF SOME TIN(II) AROMATIC THIOLATES

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SUMMARY

The reactions of tin(II) benzenethiolate and p-toluenethiolate with various fluoroaromatics in DMF have been studied. Replacement of some of the aromatic fluorines by the thiolate group was observed. The tin(II) aromatic thiolates are comparable in reactivity in these reactions with lead(II) benzenethiolate. All new compounds have been characterized by elemental analysis, and NMR (H-1 and F-19) and mass spectroscopy.

INTRODUCTION

As a continuation of the study of the reactions of the heavy metal thiolates with fluoroaromatics, some reactions of tin(II) aromatic thiolates have been examined and compared with analogous reactions of lead(II) benzenethiolate [1]. Tin(II) benzenethiolate and p-toluenethiolate were readily prepared from tin(II) acetate and the appropriate thiol [2]. Their reactions with various fluoroaromatics were studied in solution in dimethylformamide.

RESULTS AND DISCUSSION

The reactions studied are shown diagramatically ($R = C_6H_5$, $p\text{-}CH_3C_6H_5$)

$$C_6F_6 \xrightarrow{Sn(SR)_2} p\text{-}(RS)_2C_6F_4 \text{ (I); } p\text{-}F_2C_6(SR)_4 \text{ (II)}$$

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*For Part XII, see ref. 1

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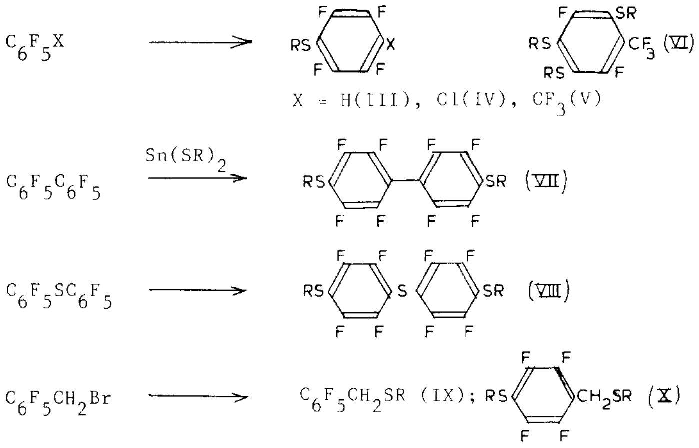

Several new compounds have been prepared using tin(II) p-toluenethiolate, namely I, IV, V, VII, VIII, IX and X (R = p-$CH_3C_6H_4$).

The reaction conditions were the same as those used for the analogous reactions of lead(II) benzenethiolate [1]. The Table shows the yields of various products using $Pb(SPh)_2$, $Sn(SPh)_2$ and $Sn(SC_6H_4CH_3)_2$ as nucleophiles The very low yield of VI and the non preparation of II from $Sn(SC_6H_4CH_3)_2$ indicate that $Sn(SC_6H_4CH_3)_2$ is probably a poorer nucleophile than $Sn(SPh)_2$ in these reactions. This difference cannot be reasonably attributed to a steric effect.

Reactions with $Sn(SPh)_2$ and $Pb(SPh)_2$ were continued until the loss of colour had indicated that the reaction was complete, and the differences in yields may be due to the losses involved in the isolation and purification of the products. The low yield reactions, forming II, IV and VII did not visually go to completion.

The tin(II) aliphatic thiolates are not as stable as the aromatic ones. Tin(II) n-heptanethiolate was prepared from the thiol and tin(II) acetate, rather than the literature method from di(methylcyclopentadienyl) tin(II) [3]. It decomposed at room temperature within one day and no substitution products, or the disulfide, $(n\text{-}C_7H_{15}S)_2$, could be isolated from its reaction with hexafluorobenzene. Tin(II) aliphatic thiolates are, therefore, not useful reagents in this type of reaction.

The reactions of pentafluorobenzyl bromide forming initially IX (mole ratio $C_6F_5CH_2Br$: $Sn(SAr)_2$, 2:1) show that the side chain bromine is more readily substituted than the aromatic fluorine.

The mechanism probably involves the formation of the thiolate anion in solution. The Sn-119 NMR spectrum of $Sn(SPh)_2$ in DMF shows that it is some-

TABLE

Reaction times and yields using $Sn(SPh)_2$, $Pb(SPh)_2$ and $Sn(SC_6H_4CH_3)_2$

Product	$Sn(SPh)_2$		$Pb(SPh)_2$*		$Sn(SC_6H_4CH_3)_2$	
	Time(h)	Yield(%)	Time(h)	Yield(%)	Time(h)	Yield(%)
I	2	25	3	75	12	21
II	120	6	24	10	–	–
III	4	94	20	95	–	–
IV	3	6	2	99	4	14
V	4	90	18†	55	3	58
VI	100	54	211	34	150	7
VII	5	16	5	88	3	9
VIII	–	–	–	–	75	9
IX	–	–	–	–	25	13
X	23	5	23	99	24	9

* See ref. 1

† No heating [1]

what soluble. Metal thiolates which are insoluble in DMF, such as CuSAr an AgSAr, do not yield fluorine substituted products in reactions with bromofluorobenzenes, but rather bromine substitution by the thiolate group is observed [4,5]. The reactions of $Pb(SPh)_2$ and $Sn(SPh)_2$ in DMF with fluoroaromatics do not give complete replacement of fluorine, as is observed with sodium thiolates in DMF [6]. This may be due to the formation of complexes of the products formed with M^{2+} ions (Sn or Pb) in solution.

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 structures were confirmed from the NMR spectra (H-1 and F-19) as described earlier [1].

From the reactions described here it can be concluded that tin(II) and lead(II) aromatic thiolates are useful synthetic reagents for the replacement of fluorine in fluoroaromatics, but are not as good as sodium aromatic thiolates. Both tin(II) and lead(II) aromatic thiolates can be stored at room temperature. The somewhat easier preparation of the lead thiolate from readily available lead(II) salts makes it a more useful reagent. The preparation of tin(II) p-toluenethiolate and tin(II) n-heptanethiolate from tin(II) acetate is much easier than the previous preparation from di(methylcyclopentadienyl)tin(II) [3].

EXPERIMENTAL

Yellow tin(II) thiolates were prepared from tin(II) acetate [7] in ethanol and a stoichiometric amount of the appropriate thiol [2]. All other reagents were available commercially. Microanalyses were performed by the Canadian Microanalytical Services Ltd., Vancouver, B.C.. The mass spectra (70 eV) were recorded on a DuPont Model 21-451 Mass Spectrometer. Infrared spectra were recorded on a Perkin Elmer Model 683 Infrared Spectrometer as KBr discs or thin films between CsBr plates. NMR spectra were recorded in $CDCl_3$ solutions on a Varian EM 360L Spectrometer (H-1 and F-19) and in DMF solution (Sn-119) on a Nicolet NT-360 Spectrometer. Data are reported relative to TMS (H-1) or $CFCl_3$ (F-19) as internal standards.

The reaction procedure was the same as that described previously for $Pb(SPh)_2$, except that 5 mmol of $Sn(SR)_2$ was used [1]. The fluoroaromatic was dissolved in 75 mL of DMF and a stoichiometric amount of $Sn(SR)_2$ to give the desired product was 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, by recrystallized from methanol vacuum sublimation, or vacuum distillation (liquids). No attempt was made to isolate any minor products.

Known compounds were characterized by comparison of their physical properties with literature values (all R = Ph): I m.p. 109.5-111° (lit. m.p. 108-111° [1]; II m.p. 133-5° (lit. m.p. 136° [1]); III b.p. 122°/6 mm (lit. b.p. 105.5°/1.8 mm [1]); IV m.p. 42-4° (lit. m.p. 39.5-41.5° [1]); V b.p. 115°/4 mm (lit. b.p. 105°/0.05mm [1]); VI m.p. 85-7° (lit. m.p. 75-7° [1]); VII m.p. 95-7° (lit. m.p. 95-6° [1]); X m.p. 84-5° (lit. m.p. 87-9° [1]).

Various new compounds, all white or pale yellow, were isolated, R = p-$CH_3C_6H_4$:

I, m.p. 116-8°. Found: C, 60.9; H, 3.59%. Calcd. for $C_{20}H_{14}F_4S_2$: C, 60. H, 3.55%. F-19 NMR: 133.3S ppm.

IV, b.p. 196°/5mm. Found: C, 50.7; H, 2.64%. Calcd. for $C_{13}H_7ClF_4S$: C, 50.8; H, 2.28%. F-19 NMR: 129.8M, 137.9M pp.: intensity ratio 1:1.

V, m.p. 40-1°. Found: C, 49.4; H, 1.95%. Calcd. for $C_{14}H_7F_5S$: C, 49.4; H, 2.06%. F-19 NMR: 56.8T (CF_3), 132.5M (ArF), 141.0M (ArF) ppm.: intensity ratios 3(CF_3):2(ArF):2(ArF);J(CF_3-ArF_{ortho}) 21.8; J(ArF-F_{ortho}) 24.2; J(ArF-F_{para}) 13.2 Hz.

VI, m.p. 87-9°. Found: C, 61.3; H, 3.83%. Calcd. for $C_{28}H_{21}F_5S_3$: C, 61.3; H, 3.87%. F-19 NMR: 44.2D (CF_3), 80.21D (ArF), 93.4DQ (ArF) ppm.: intensity ratios 3(CF_3):1ArF:1ArF. J(CF_3-ArF_{ortho}) 34.8; J(ArF-F_{para}) 18.8 Hz

VII, m.p. 116-8°. Found C, 57.3; H, 2.51%. Calcd. for $C_{26}H_{14}F_8S_2$: C, 57.6; H, 2.58%. F-19 NMR:130.0M, 134.7M ppm.: intensity ratio 1:1.

VIII, m.p. 151-2°. Found: C, 54.2; H, 2.48%. Calcd. for $C_{26}H_{14}F_8S_3$: C, 54.4; H, 2.44%. F-19 NMR: 134.0M ppm..

IX, m.p. 52-4°. Found: C, 55.3; H, 3.07%. Calcd. for $C_{14}H_9F_5S$: C, 55.3; H, 2.96%. F-19 NMR: 139.6M, 158.7TT, 166.1M ppm.: intensity ratios 2:1:2. H-1 NMR: 4.00S (-CH_2SR).

X, m.p. 76-8°. Found: C, 62.3; H, 4.05%. Calcd. for $C_{21}H_{16}F_4S_2$: C, 61.8; H, 3.95%.

All the H-1 NMR spectra of the compounds containing the p-toluenethiolate group showed signals at approximately 2.3S ppm. and 7.1M ppm., corresponding to the CH_3 group and the aromatic protons respectively.

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