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SOME DERIVATIVES OF 2,3,5,6-TETRAFLUOROBENZENETHIOL

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SUMMARY

Various metallic and organometallic derivatives of 2,3,5,6-tetrafluorobenzenethiol have been prepared directly from the thiol. Its Cu(I) and Pb(II) salts were converted into thioethers and thioesters. All new compounds have been characterized by elemental analysis, NMR (H-1 and F-19) and mass spectroscopy.

INTRODUCTION

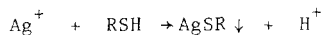
2,3,5,6-Tetrafluorobenzenethiol, $\text{C}_6\text{F}_4\text{SH}$, has been further examined [1]. Readily prepared from pentafluorobenzene and sodium hydrogen sulfide it is a liquid at room temperature, b.p. 147° [1]. With diazomethane it gave the methyl thioether and by oxidation the disulfide, $(\text{C}_6\text{F}_4\text{HS})_2$ [1]. Potassium tetrafluorobenzenethiolate has been used as a nucleophile in reactions with various haloaromatics [2]. Several derivatives of the thiol have been prepared by the nucleophilic displacement of fluorine in pentafluorobenzene with thiolate anions, RS^- [1,2,3,4]. The reactions of copper(I)



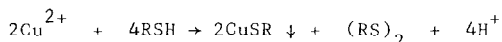
thiolates with bromofluorobenzenes can yield compounds containing the 2,3,5,6-tetrafluorophenylthio group [5,6] and tetraphenylporphyrin iron(III) derivative containing it are known [7,8]. This paper described the preparation of some metallic, organometallic and organic derivatives of 2,3,5,6-tetrafluorobenzenethiol.

RESULTS AND DISCUSSIONS

Many metallic thiolates precipitate when an aqueous solution of the metal ion is stirred with a suspension of a liquid thiol or a solution of thiol in a water immiscible organic solvent [9]. It has been possible

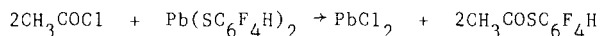


to prepare the thiolates, $\text{M}(\text{SC}_6\text{F}_4\text{H})_x$, $\text{M} = \text{Cu(I)}, \text{Ag(I)}, \text{Au(I)}, \text{Tl(I)}, \text{Cd(II)}$, $\text{Hg(II)}, \text{Pd(II)}, \text{Pt(II)}$ and Pb(II) , by this method. In some cases, such as copper(II), the thiol acts as a reducing agent and copper(I) thiolate is formed, together with the disulfide. Other metallic and organometallic

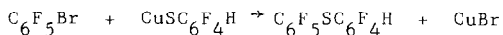
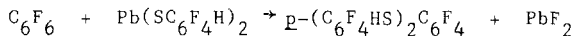


thiolates were prepared by appropriate literature methods, using the thiol; $\text{Ni}(\text{SC}_6\text{F}_4\text{H})_2$ [10], $\text{Zn}(\text{SC}_6\text{F}_4\text{H})_2$ [10], $\text{Sn}(\text{SC}_6\text{F}_4\text{H})_2$ [11], $\text{Ph}_3\text{MSC}_6\text{F}_4\text{H}$ ($\text{M} = \text{Sn}, \text{Pb}$) [12,10], $\text{Bu}_3\text{SnSC}_6\text{F}_4\text{H}$ [12] and $\text{Bu}_2\text{Sn}(\text{SC}_6\text{F}_4\text{H})_2$ [12]. These reactions are similar to those observed for both benzenethiol and the fully fluorinated pentafluorobenzenethiol. They show the somewhat acidic nature of the thiol proton.

Lead(II) and copper(I) thiolates are useful reagents for the preparation of organic derivatives of thiols [13,7]. The monothioesters $\text{RCOSC}_6\text{F}_4\text{H}$ ($\text{R} = \text{Me}, \text{Ph}$) were obtained from the acyl chloride and lead(II) thiolate [13]; the methylthioether, $\text{MeSC}_6\text{F}_4\text{H}$, was prepared analogously from methyl iodide.

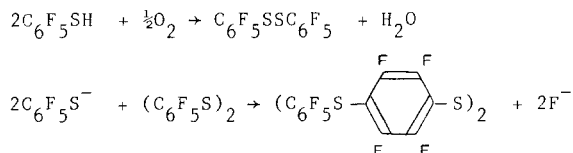


A thiolate group can be introduced onto an aromatic ring by displacement of fluorine using lead thiolate in DMF [14] or by displacement of bromine or iodine in bromo(iodo)fluorobenzenes with copper(I) thiolates in DMF [6]. Lead(II) and copper(I) tetrafluorobenzenethiolates have been used in this way.



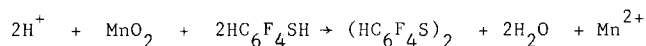
These reactions demonstrate the anticipated synthetic utility of these two metal thiolates.

Pentafluorobenzenethiol is known to polymerize, particularly in alkaline solution in air. It has been postulated that this reaction occurs by initial oxidation of the thiol and subsequent nucleophilic attack by the thiolate anion, formed in the alkaline solution [10].



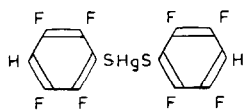
This polymerization also occurs when lead(II) pentafluorobenzenethiolate is handled in warm DMF.

Various attempts to polymerize 2,3,5,6-tetrafluorobenzenethiol were unsuccessful. In all cases the reaction stopped at the disulfide stage.



The only structural difference between these two thiols is in the position para to the thiol group and the mechanism postulated for the polymerization of pentafluorobenzenethiol is confirmed [10].

The new compounds isolated have been characterized by elemental analysis, mass spectroscopy (when sufficiently volatile) and, partially, by NMR spectroscopy, both H-1 and F-19. The 2,3,5,6-tetrafluorophenylthio group shows characteristic spectra in both the aromatic proton region and in the fluorine spectrum [3]. For example in the compound $\text{Hg}(\text{SC}_6\text{F}_4\text{H})_2$, the aromatic



proton is split into a triplet of triplets due to couplings to the two ortho fluorines ($J \sim 10\text{Hz}$) and two meta fluorines ($J \sim 7\text{Hz}$). In the fluorine spectrum two signals are observed, of relative intensity 1:1, each split into eight lines due to couplings involving the ortho fluorine ($J \sim 24\text{Hz}$), the para fluorine ($J \sim 12\text{Hz}$) and the aromatic hydrogen. The structure of the compound $\text{p}-(\text{C}_6\text{F}_4\text{HS})_2\text{C}_6\text{F}_4$, is demonstrated unequivocally from its fluorine spectrum where two multiplets and a singlet of equal intensity, are observed.



Details of some NMR spectra are shown in Table 1.

From the reactions described here it can be concluded that the properties of 2,3,5,6-tetrafluorobenzenethiol are as expected for an aromatic thiol. The main difference from pentafluorobenzenethiol was its non polymerization. The metal salts, $\text{Pb}(\text{SC}_6\text{F}_4\text{H})_2$ and $\text{CuSC}_6\text{F}_4\text{H}$ have both been shown to be useful synthetic reagents.

EXPERIMENTAL

All reagents were available commercially. 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. Mass spectra (70 eV) were recorded on a DuPont Model 21-451 Mass Spectrometer, using a direct introduction technique. The NMR spectra of CDCl_3 solutions were recorded on a Varian EM 360 L NMR Spectrometer, using TMS (H-1) and $\text{F}_3\text{CCO}_2\text{H}$ (F-19) as internal and external standards respectively.

All reactions were studied on the 5-10 mmol scale. Metal thiolates were prepared by adding a stoichiometric amount of the neat liquid thiol to a well stirred aqueous solution of the metal salt. The precipitated thiol was washed with water and hexane [9]. All other products were prepared by literature methods starting from the thiol. Known compounds were identified by comparison of m.p. or b.p. with literature values: $\text{CH}_3\text{SC}_6\text{F}_4\text{H}$, yield 10%, b.p. $64^\circ/4$ mm Hg (lit. b.p. $167-74^\circ/760$ mm Hg [1]); $p\text{-(C}_6\text{F}_4\text{HS)}_2\text{C}_6\text{F}_4$ yield 20%, m.p. $154-5^\circ$ (lit. m.p. 157° [2]); $(\text{HC}_6\text{F}_4\text{S})_2$ yield 90% from Cu^{2+} and $\text{C}_6\text{F}_4\text{HSH}$, m.p. $38-9^\circ$ (lit. m. p. 38° [2]).

ACKNOWLEDGEMENTS

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TABLE 1
NMR Spectra

| Compound | Chemical Shift* (ppm) | Coupling Constants (Hz) |
|----------|----------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| | 7.16 TT (ArH) 136.8 M (F _a) 132.2 M (F _b) | J(H-F _a) 9.5 : J(H-F _b) 7.2 J(F-F _{ortho}) 22.4 : J(F-F _{para}) 11.1 : J(F-H) 9.9 J(F-F _{ortho}) 24.4 : J(F-F _{para}) 12.2 : J(F-H) 7.5 |
| | 0.88 TT (Me) 1.56 M (CH ₂) 6.89 TT (ArH) 138.5 M (F _a) 131.8 M (F _b) | J(CH ₃ -CH ₂) 5.6 J(H-F _a) 9.5 : J(H-F _b) 7.2 J(F-F _{ortho}) 23.5 : J(F-F _{para}) 11.3 : J(F-H) 9.4 J(F-F _{ortho}) 24.0 : J(F-F _{para}) 11.8 : J(F-H) 7.5 |
| | 0.96 T (Me) 1.36 M (CH ₂) 6.80 TT (ArH) 139.5 M (F _a) 132.0 M (F _b) | J(CH ₃ -CH ₂) 4.6 J(H-F _a) 10.1 : J(H-F _b) 7.4 J(F-F _{ortho}) 24.1 : J(F-F _{para}) 11.7 : J(F-H) 9.4 J(F-F _{ortho}) 24.7 : J(F-F _{para}) 11.9 : J(F-H) 7.5 |
| | 7.26 TT (ArH) 141.8 M (F _a) 133.9 M (F _b) | J(H-F _a) 10.1 : J(H-F _b) 7.4 J(F-F _{ortho}) 24.4 : J(F-F _{para}) 12.4 : J(F-H) 10.3 J(F-F _{ortho}) 24.2 : J(F-F _{para}) 11.7 : J(F-H) 7.5 |
| | 2.50 T (Me) 7.02 TT (ArH) 139.2 M (F _a) 131.2 M (F _b) | J(CH ₃ -F _{ortho}) 1.4 J(H-F _a) 10.0 : J(H-F _b) 7.1 J(F-F _{ortho}) 24.0 : J(F-F _{para}) 11.9 : J(F-H) 10.0 J(F-F _{ortho}) 23.9 : J(F-F _{para}) 12.5 : J(F-H) 7.2 : J(F-Me) 1.5 |
| | 7.11 TT (ArH) 137.2 M (F _a) 132.7 M (F _b) 132.2 S (F _c) | J(H-F _a) 9.5 : J(H-F _b) 7.3 |
| | | |

* Corrected to CFCl₃ as internal standard.

TABLE 2

Physical Properties, yields and chemical analyses of new compounds

| Compound | Color | m.p. (°C) b.p. (°C/kPa) | Method [†] | Yield (%) | Found (%) | | Calculated (%) | |
|-------------------------------------|-----------|----------------------------|---------------------|-----------|-----------|-------|----------------|------|
| | | | | | C | H | C | H |
| CuSR* | yellow | >300 | A | 93 | 29.0 | <0.3 | 29.4 | 0.41 |
| AgSR | white | >300 | A | 85 | 24.9 | 0.11 | 24.9 | 0.35 |
| AuSR | beige | 244 (d) | A | 70 | 19.0 | <0.2 | 19.1 | 0.26 |
| Zn(SR) ₂ | white | >300 | B | 84 | 33.8 | 0.76 | 33.9 | 0.47 |
| Cd(SR) ₂ | white | >300 | A | 80 | 30.4 | 0.24 | 30.4 | 0.43 |
| Hg(SR) ₂ | white | 195-6 | A | 95 | 25.5 | <0.3 | 25.6 | 0.36 |
| Ni(SR) ₂ | deep red | >300 | B | 96 | 34.2 | <0.42 | 34.4 | 0.48 |
| Pd(SR) ₂ | red-brown | 250 (d) | A | 75 | 30.8 | 0.27 | 30.9 | 0.43 |
| Pt(SR) ₂ | yellow | >300 | A | 90 | 25.5 | <0.3 | 25.9 | 0.36 |
| Pb(SR) ₂ | lt. green | >300 | A | 75 | 25.3 | 0.21 | 25.3 | 0.35 |
| TlSR | white | >300 | A | 40 | 19.4 | <0.3 | 18.7 | 0.26 |
| Sn(SR) ₂ | yellow | 210 (d) | C | 78 | 29.4 | 0.35 | 30.0 | 0.42 |
| Ph ₃ PbSR | white | 116-8 | B | 96 | 46.5 | 2.35 | 46.8 | 2.60 |
| Ph ₃ SnSR | white | 123-4 | D | 42 | 54.3 | 3.04 | 54.3 | 2.92 |
| Bu ₂ Sn(SR) ₂ | white | 47-8 | D | 50 | 40.0 | 3.35 | 40.4 | 3.39 |
| Bu ₃ SnSR | colorless | 142.5/0.09 | D | 65 | 45.9 | 6.04 | 45.9 | 5.99 |
| MeCOSR | yellow | 42.0/0.20 | E | 47 | 42.7 | 1.79 | 42.7 | 1.79 |
| PhCOSR | white | 53-5 | E | 68 | 54.6 | 2.11 | 54.5 | 1.93 |
| C ₆ F ₅ SR | white | 52-5 | F | 10 | 41.1 | <0.5 | 41.4 | 0.29 |

*R = HC₆F₄[†] Modified literature methods: A[9], B[10], C[11], D[12], E[13], F[6].

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