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SOME REACTIONS OF COPPER(I) PENTAFLUOROTHIOPHENOLATE

MICHAEL E. PEACH and ANNA M. RITCEY

Chemistry Department, Acadia University, Wolfville, Nova Scotia,
B0P 1X0, (Canada)

SUMMARY

Copper(I) pentafluorothiophenolate, $CuSC_6F_5$ reacted with a number of acyl and alkyl halides in either n-hexane or DMF. The products $RCH_2SC_6F_5$ (R = Me, Ph, C_6F_5S, $C_6F_5SCH_2$), $Ph_2CHSC_6F_5$, $R_3CSC_6F_5$ (R =Me, Ph) and $RCOSC_6F_5$ (R = Me, C_6F_5) have been characterized and their spectra, particularly NMR spectra (H-1, C-13, F-19) have been examined.

INTRODUCTION

Copper(I) thiolates react with a large number of aromatic halides in solvents such as DMF (N,N-dimethylformamide) [1,2]. The ease of halogen replacement is I>Br>Cl. As the copper(I) thiolates are readily prepared [3,4], the reactions of the specific thiolate copper(I) pentafluorophenylthiolate with various aliphatic and acyl halides has been investigated as a continuation of the study of pentafluorothiophenol and its derivates [5].

RESULTS AND DISCUSSION

Lead(II) pentafluorothiophenolate, $Pb(SC_6F_5)_2$, reacts with alkyl and acyl halides using either an inert solvent or an excess of the alkyl halide [6]. Copper(I) pentafluorothiophenolate reacted with some of the more reactive alkyl halides and some acyl halides in n-hexane, although

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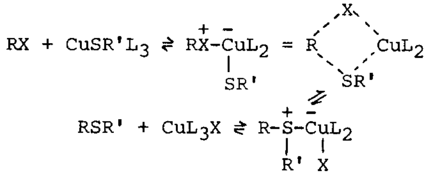
$$\begin{array}{lll}
Ph_3CCl + CuSC_6F_5 & \rightarrow & Ph_3CSC_6F_5 + CuCl \\
Ph_2CHBr + CuSC_6F_5 & \rightarrow & Ph_2CHSC_6F_5 + CuBr \\
PhCH_2Br + CuSC_6F_5 & \rightarrow & PhCH_2SC_6F_5 + CuBr \\
Me_3CCl + CuSC_6F_5 & \rightarrow & Me_3CSC_6F_5 + CuCl \\
MeCOCl + CuSC_6F_5 & \rightarrow & MeCOSC_6F_5 + CuCl \\
C_6F_5COCl + CuSC_6F_5 & \rightarrow & C_6F_5COSC_6F_5 + CuCl
\end{array}$$

the reactions with C_6F_5COCl and $PhCH_2Br$ refluxing was needed. The less reactive alkyl halides would not react in n-hexane, but did in DMF.

$$\begin{array}{lll}
EtI + CuSC_6F_5 & \rightarrow & EtSC_6F_5 + CuI \\
Br_2CH_2 + 2CuSC_6F_5 & \rightarrow & (C_6F_5S)_2CH_2 + 2CuBr \\
(BrCH_2)_2 + 2CuSC_6F_5 & \rightarrow & C_6F_5SCH_2CH_2SC_6F_5 + 2CuBr
\end{array}$$

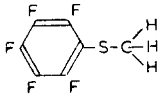
The DMF must be postulated to participate in the reaction involving a mechanism such as



L = DMF

Such a reaction pathway has been postulated previously for the reactions of various aryl halides [7]. Under similar conditions CH_2Cl_2 and $ClCH_2CH_2Cl$ did not react. These reactions show that, although the yields were sometimes not very good, copper(I) thiolates, specifically $CuSC_6F_5$, can be used in reactions with aliphatic halides.

The NMR spectra of the products are reported in Tables 1 and 2. The fluorine spectra were analyzed as described previously [9]. The spectra all confirm the structures of the product. In compounds such as C_6F_5SMe the methyl protons are coupled to the ortho-fluorines and a through space mechanism has been postulated [10].



J(H-F) = 0.7 Hz

In the C-13 spectrum of C_6F_5SMe the methyl carbon is observed to be coupled to the ortho fluorine (J(C-S-C-C-F) 3.14Hz) [11]. Some of the compounds described here can be categorized as $C_6F_5SCH_2X$, $C_6F_5SCHX_2$, $C_6F_5SCX_3$. In no cases was any coupling of the methylene or methyne protons

TABLE 1

Summary of NMR data

Compound	Chemical Shifts (p.p.m.)				
	H	F-2,6	F-3,5	F-4	C*
$CH_3COSC_6F_5$	2.39S (CS_2)	132.2M	161.8M	150.5TT	29.86S (CH_3) 188.75S (CO)
$(C_6H_5)_3CSC_6F_5$	7.25M	126.8M†	162.6M†	151.4TT†	77.05S
$(C_6H_5)_2CCHSC_6F_5$	5.60S (CS_2) 7.22M	133.9M	162.8M	153.5TT	
$C_6H_5CH_2SC_6F_5$	3.99S 7.16S	133.9M	163.1M	154.5TT	39.43S
$(CH_3)_3CSC_6F_5$	1.32S (CS_2)	130.5M	162.6M	152.5TT	
$CH_3CH_2SC_6F_5$	1.29T (CS_2) 3.88Q	133.2M §	162.3M §	154.4TT §	
$(C_6F_5S)_2CH_2$	4.30S	133.7M	162.0M	152.2TT	39.14Q
$(C_6F_5SCH_2)_2$	3.01S	134.3M	162.7M	153.8TT	34.72S

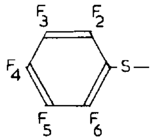
All spectra recorded in $CDCl_3$ or $CHCl_3$ solution with TMS or F_3CO_2H (corrected to $CFCl_3$) as internal standard, unless indicated.

S = singlet T = triplet M = multiplet

*C-13 of C-SC_6F_5

†Recorded in CCl_4 [6]

§Recorded in C_6H_6 [8]



to the ortho fluorine observed. This may be due to hindered rotation about the C-S bonds, reducing the coupling to less than about 0.5Hz, when it could not be resolved. Similarly no coupling of the methylene or methyne carbon to the ortho fluorine was observed, except in $C_6F_5SCH_2CH_2SC_6F_5$ when an unexplained quartet (J∿1.7Hz) was found.

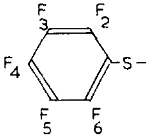
In most cases the mass spectra of the products confirm the molecular weights. The $C_6F_5S^+$ ion and its subsequent fragmentation were major features of the spectra. This is a major feature of the mass spectra of some aliphatic and acyl derivatives of pentafluorothiophenol [12].

The infrared spectra of the products confirmed the presence of various functional groups.

TABLE 2

Fluorine-fluorine coupling constants

Compound	Coupling constants (HZ)					
	J(2,3)	J(3,4)	J(2,4)	J(3,5)	J(2,6)	J(2,5)
$CH_3COSC_6F_5$	22.8	20.4	3.3	1.3	5.1	7.8
$(C_6F_5S)_2CH_2$	23.8	20.4	2.8	1.0	3.8	8.4
$(C_6F_5SCH_2)_2$	22.5	20.4	2.4	1.1	3.6	7.9
$C_2H_5SC_6F_5$ [8]	24.0	20.5	2.1	2.0	2.7	8.3
$C_6H_5CH_2SC_6F_5$	25.3	20.7	2.4	1.4	3.3	9.0
$(C_6H_5)_2CHSC_6F_5$	24.4	20.7	2.5	1.8	5.2	8.0
$(CH_3)_3CSC_6F_5$	25.5	20.4	3.1	1.0	2.8	9.0



EXPERIMENTAL

All the reagents were available commercially, except $CuSC_6F_5$ and $Pb(SC_6F_5)_2$ which were prepared by standard methods [3]. Microanalyses were performed by Canadian Microanalytical Services Ltd., Vancouver, B.C.

The 70eV mass spectra were recorded on a DuPont 21-491 mass spectrometer using direct introduction. The NMR spectra were recorded on a Varian EM 360L NMR spectrometer or a Varian CFT-20 (C-13 and some H-1). The infrared spectra were recorded as KBr discs or thin films on a Perkin-Elmer 683 Infrared Spectrophotometer.

Method A was tried initially for all reactions. The appropriate amount of organic halide was added to a suspension of 10 mmol of $CuSC_6F_5$ in 50 mL n-hexane. The course of the reaction at room temperature was followed visually. When complete, the precipitated copper halide was filtered off and the product isolated by evaporation of the solvent.

Method B was similar to method A but involved refluxing the n-hexane for 5h (C_6F_5COCl) and 30 min ($C_6H_5CH_2Br$).

Method C was analogous, but refluxing DMF was used as a solvent and the reaction quenched by pouring onto ice/water from which the product was extracted with ether.

The following known compounds were prepared $MeCOSC_6F_5$, method A, yield 12%, b.p. 46°/<1.3KPa, lit. b.p. 92°/2.3KPa [6]; $Ph_3CSC_6F_5$, method A, yield 65%, m.p. 128-9°, lit. m.p. 120-1° [6]; $C_6F_5COSC_6F_5$, method B, yield 24%, m.p. 60-1°, lit. m.p. 57-9° [6]; $(C_6F_5S)_2CH_2$, method C, yield 10%, m.p. 64-5°, lit 65° [6]; $C_6F_5SCH_2CH_2SC_6F_5$, method C, yield 8%, m.p. 136-7° lit. 139-140° [6]; $EtSC_6F_5$, method C, yield 15%, b.p. 181-3°, lit. b.p. 72°/0.3KPa [12].

New compounds isolated: $Ph_2CHSC_6F_5$, method A, white m.p. 66-7°, yield 47% (recrystallized from EtOH and vacuum sublimed: found, C, 62.4; H, 2.95; S, 8.53; calcd. C, 62.3; H, 3.03; S, 8.75%, :$Me_3CSC_6F_5$, method A, white, m.p. 33-4°, yield 22%, (purified by column chromatography and vacuum distillation); found, C 53.3; H, 1.78; S, 11.1; calcd. C, 53.8; H 2.43; S, 11.1%; $PhCH_2SC_6F_5$, method B, white, m.p. 43-4°, yield 31% (recrystallized from EtOH), found C, 47.0; H, 3.26; S, 12.7; calcd. C, 46.9; H, 3.54; S, 12.5%.

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