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REACTIONS OF SOME BROMOFLUOROBENZENES WITH COPPER(I) BENZENETHIOLATE

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SUMMARY

The reactions of copper(I) benzenethiolate with some bromofluorobenzenes have resulted in the replacement of the bromine by a phenylthio group. Combinations of this method and the reactions of sodium thiolates with fluorobenzenes have enabled various isomeric phenylthio substituted fluorobenzenes $C_6H_xF_y(SR)_z$ to be prepared. The new products have been characterized by elemental analyses, mass, infrared, and fluorine NMR spectroscopy.

INTRODUCTION

The two different halogen atoms in bromofluorobenzenes can be replaced by thiolate groups. The fluorine, but not the bromine, is substituted using sodium thiolate or a similar thiolate, while exclusive replacement of the bromine occurs with copper(I) thiolate in DMF [1]. Protodebromination may be observed in both of these reactions.

Copper(I) thiolates are easily prepared and some of the reactions of $CuSCF_3$ [2,3], $CuSC_6F_5$ [4,5,6], CuSMe [1], CuSBu [7,8,9,10] and CuSPh [9,10] with haloaromatics have been studied. The reactions of copper(I) n-butanethiolate were solvent dependent, giving exclusive bromine replacement in DMF, and fluorine replacement coupled with protodebromination in DMF with thiourea added. An appropriate mechanism has been postulated [8]. The reactions of copper(I) benzenthiolate with bromofluorobenzenes have not been studied, although the reactions of bromopentafluorobenzene with $CuSC_6F_5$ [4], CuSBu [8] and the reactions of some dibromotetrafluorobenzenes with CuSMe [1] and $CuSC_6F_5$ [6] have been examined.

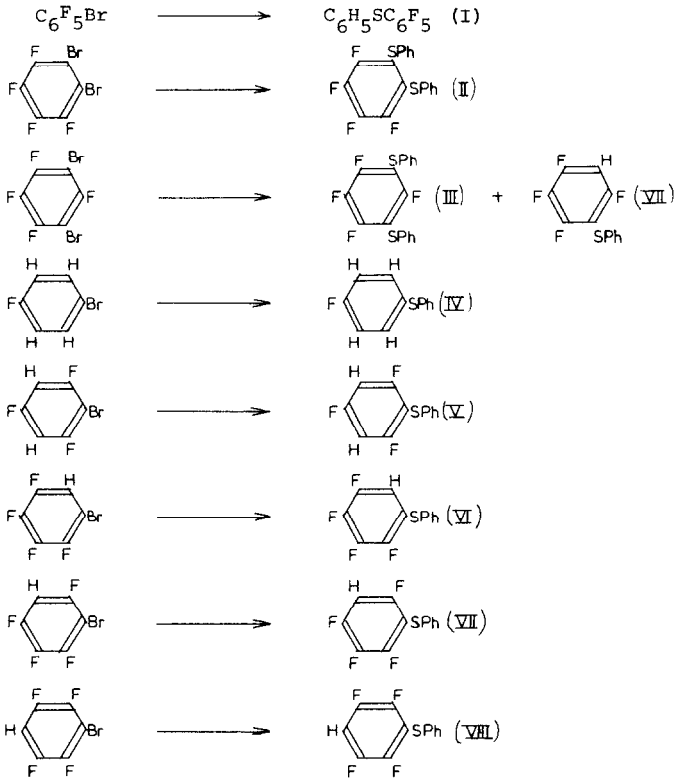
Previous studies on the reactions of sodium methanethiolate with various fluoroaromatics have produced a series of methylthio substituted fluorobenzenes [11,12,13]. Partial replacement of the fluorine occurred using an ethylene glycol/pyridine mixture as solvent, whereas complete substitution occurred using DMF as solvent [11,13].

The reactions of hexafluorobenzene with the methanethiolate and benzenethiolate anions in ethylene glycol/pyridine gave p-$(RS)_2C_6F_4$ and p-$F_2C_6(SR)_4$ [11].

$$C_6F_6 + SR^- \rightarrow \text{p-}(RS)_2C_6F_4 \text{ and p-}F_2C_6(SR)_4 \qquad (R = Me, Ph)$$

The other isomers o-$(RS)_2C_6F_4$ and m-$(RS)_2C_6F_4$ (R = Me, C_6F_5) have been prepared from o-$Br_2C_6F_4$ and m-$Br_2C_6F_4$ and copper(I) thiolates [1,6].

As an extension of this work the reactions of a series of bromofluorobenzenes with copper(I) benzenethiolate have been studied. The results are summarized below.

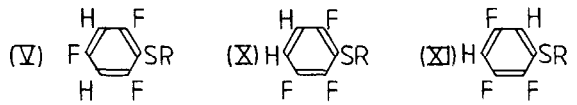


RESULTS AND DISCUSSION

The compound I is well known, and has been prepared from pentafluorobromobenzene, n-butyl lithium and diphenyldisulfide [14] , or pentafluorobenzenesulfenyl chloride and phenyl magnesium bromide [15] . The preparation described here is as convenient as either of these methods.

All of the isomers of tetrafluoro(phenylthio)benzene, $F_4(PhS)C_6H$, namely VI, VII, and VIII can be prepared by the method described here. The para isomer, VIII, can also be obtained from pentafluorobenzene and sodium benzenethiolate [12,16] , and the ortho isomer, VI, from tetrafluorobenzyne and thioanisole [17] . Similarly all the isomers of tetrafluorobis(phenylthio)benzene, $F_4(PhS)_2C_6$, have been isolated. The preparation of the ortho and meta isomers, II and III, is described here, while the para isomer is readily obtained from hexafluorobenzene and sodium benzenethiolate [11,18]

It should be possible to prepare all the substituted alkylthio- and arylthio-fluorobenzenes by judicious selection of the reactions of either an appropriate fluorobenzene with a sodium thiolate or an appropriate bromofluorobenzene with a copper (I) thiolate. In the series of alkylthio- or arylthio-trifluorobenzenes, $F_3(RS)C_6H_2$, isomer V (R = Ph) has been



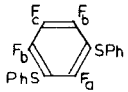
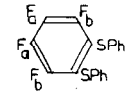
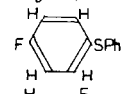
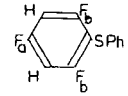
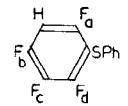
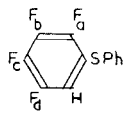
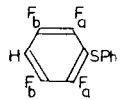
described here and the isomers X and XI (R = Me) can be obtained by displacement by the methanethiolate anion of one fluorine atom from the appropriate tetrafluorobenzene [12] . It should be possible to prepare the other isomers of $F_3(RS)C_6H_2$ from the appropriate bromotrifluorobenzene and a copper (I) thiolate.

The new compounds isolated have been characterized by elemental analysis, fluorine NMR and mass spectroscopy. The mass spectra confirm the molecular weights. The fluorine NMR spectra, summarized in Table 1, are all first order, except II which is an A_2B_2 spectrum. The coupling constants are consistent with the literature values and with those observed in analogous compounds [12] . The fluorine NMR spectrum of I has been reported[15] . The infrared spectra confirm the presence of the various functional groups.

Only the primary ion mass spectra were examined. In this study two isomeric series have been prepared. Previous studies on the isomeric series $C_6F_xH_y(SMe)$ and $C_6F_xH_y(NH_2)SMe$ showed that the primary ion spectra could not be used to distinguish between isomers [12,19] . Similarly little difference

TABLE 1

Fluorine NMR Spectra

Compound	Chemical Shift* (ppm)	Coupling Constants (Hz)
	100.04(F_a)	J(F-F_m) 1.6; J(F-F_p) 11.3
	122.42(F_b)	J(F-F_o) 23.4; J(F-F_m) 1.7
	161.20(F_c)	J(F-F_o) 23.9; J(F-F_p) 11.5
	152.98(F_a) 125.97(F_b)	J(F_a-F_a) 19.6; J(F_a-F_b) 23.3; J(F-F_m) 4.8; J(F-F_p) 11.8
	113.81	J(F-H_o) 8.5; J(F-H_m) 5.4
	105.01(F_a)	J(F-F_m) 8.3; J(F-H_o) 8.3
	100.31(F_b)	J(F_b-F_a) 8.0; J(F_b-F_b) 1.9; J(F-H_o) 6.2; J(F-H_p) 1.9
	107.65(F_a)	J(F_a-F_b) 3.4; J(F-F_p) 11.4; J(F-H_o) 8.1
	130.00(F_b)	J(F-F_o) 21.5; J(F_b-F_d) 7.7; J(F_b-F_a) 3.5; J(F-H_o) 10.2
	163.37(F_c)	J(F_c-F_d) 23.1; J(F_c-F_b) 21.4; J(F-F_p) 11.3; J(F-H_m) 6.1
	123.96(F_d)	J(F-F_o) 23.0; J(F_d-F_b) 7.7; J(F-H_p) 2.4
	134.96(F_a)	J(F-F_o) 21.3; J(F-F_m) 3.2; J(F-F_p) 11.8; J(F-H_m) 6.3
	155.12(F_b)	J(F_b-F_a) 21.4; J(F_b-F_c) 19.5; J(F-F_m) 2.5; J(F-H_p) 2.5
	157.38(F_c)	J(F_c-F_d) 20.9; J(F_c-F_b) 19.6; J(F-F_m) 3.1; J(F-H_m) 8.0
	139.11(F_d)	J(F-F_o) 21.0; J(F-F_m) 2.6; J(F-F_p) 11.8; J(F-H_o) 10.3
	133.06(F_a)	J(F-F_o) 21.4; J(F-F_m) 1.8; J(F-F_p) 10.5; J(F-H_m) 7.3
	138.11(F_b)	J(F-F_o) 21.4; J(F-F_p) 10.5; J(F-H_o) 9.6

* Relative to $CFCl_3$ as the internal standard.

was observed in the primary ion spectra of the isomers of $C_6F_4H(SPh)$, VI, VII, and VIII. Some potentially significant differences in the spectra of the isomers of $C_6F_4(SPh)_2$, II and III were observed. These will be examined further.

EXPERIMENTAL

All the reagents were available commercially, except CuSPh which was prepared from C_6H_5SH and $CuSO_4$ [20]. Microanalyses were performed by the Canadian Microanalytical Services Ltd., Vancouver, B. C. or Mikroanalytisches Laboratorium, Beller, Göttingen, W. Germany. The analytical data and physical properties of the new compounds are shown in Table 2.

TABLE 2

Products and Chemical Analyses

Compound	m.p./°C b.p./°C/kPa	Calculated (%) C	H	Found (%) C	H	Yield (%)	Purification†
II	62.5-64.0	59.0	2.75	59.3	2.36	67	1
III	115/0.27	59.0	2.75	59.8	3.02	62	2,3
IV	171/3.20	70.6	4.44	70.2	4.35	83	2
V	154/4.93	60.0	2.94	59.8	2.75	42	2
VI	169/4.40 §	55.8	2.34	55.9	2.37	77	2
VII‡	179/3.20	55.8	2.34	56.0	2.45	56	2,3
VIII	159/3.60*	55.8	2.34	55.9	2.32	55	2

* Lit. b.p. 265°C/101 kPa [16]

† 1 = Recrystallization MeOH; 2 = vacuum distillation; 3 = column chromatography

‡ S = (Found), 12.5; (Calc.) 12.4%

§ Lit. m. p. 52°C 17

The mass spectra (82 eV) were recorded on a DuPont Model 21-451 Mass Spectrometer using a direct introduction technique. The (70 eV) mass spectrum of $\underline{o}$-$C_6F_4(SPh)_2$ was recorded on a DuPont Model 21-104 Mass Spectrometer. Infrared spectra were recorded on a Perkin Elmer Model 457 spectrometer between CsBr plates or as KBr discs. The NMR Spectra of $CDCl_3$ solutions were recorded on a Varian HA-100 using $FCCl_3$ as the internal standard.

The reactions of the bromofluorobenzenes with CuSPh were studied by one general method, outlined below.

The appropriate bromofluorobenzene starting material (20 mmol) was dissolved in 75 mL DMF and heated for 0.25 h at 140°C. A 50% excess of

CuSPh was added to the hot solution and the mixture was stirred and refluxed for a suitable period. The reactions of $\underline{o}$-$C_6F_4Br_2$ and $\underline{m}$-$C_6F_4Br_2$ were refluxed for two hours, whereas the other bromofluorobenzenes required a longer reaction time (23 h) to produce the desired products. The hot reaction mixture was quenched by pouring onto a mixture of 400 g ice and 250 mL concentrated hydrochloric acid. This solution was extracted twice with 200 mL portions of diethyl ether. The ether extract was filtered when necessary to remove any insoluble materials, and dried over anhydrous magnesium sulfate for approximately 24 h. The extract was then filtered and the crude products were isolated from the filtrate by removal of the ether.

The majority of the products were either colorless or pale yellow liquids and were purified by two or three vacuum distillations. Purities of all the products were checked with thin layer chromatography. When minor products persisted, further purification was achieved by column chromatography using silica gel as the stationary phase and 15% ether/hexane as the eluent. In the reaction of $\underline{m}$-$Br_2C_6F_4$ some protodebromination occurred and some VII was formed. A minor impurity was present in VII, otherwise the major product was the only product. I was obtained in 75% yield and identified by its m.p. [14].

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