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THE PREPARATION AND REACTIONS OF SOME DIMETALLIC COMPOUNDS DERIVED FROM TETRACHLOROTHIOPHENE

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SUMMARY

The use of tetrachlorothiophene in the preparation of several dimetallic derivatives is described. Thus, 2,5-dilithiodichlorothiophene was prepared in nearly quantitative yield via a halogen–metal exchange reaction between n-butyllithium and tetrachlorothiophene. This dilithio compound was converted, also in satisfactory yield, to a dicopper derivative by reaction with CuCl or CuI in a mixture of tetrahydrofuran and ether at low temperature. Some derivatives of each of the dimetallic compounds were prepared, and among characterizations were those of IR, NMR, and mass spectrometry.

INTRODUCTION

Our previous work on the Grignard reagent[1], lithium[2] and copper[3] derivatives of tetrachlorothiophene had shown these to be of utility in preparing organosilicon compounds[1,2] and ketones[3] as well as iodo compounds[4]. In the preparation of the lithium compound[2], there was some evidence that a dilithio derivative had also been formed in low yield*.

Several di- and tri-lithio derivatives of perhalogenated benzenes have been prepared[5-12] by both halogen–metal exchange and metalation reactions. Among dilithio derivatives of thiophenes are 2,5-dilithiothiophene[13], 3,4-dilithiothiophene[14] and 2,5-dilithiodibromothiophene[15]. There is good evidence that 2,5-bis(bromomagnesium)dibromothiophene has also been prepared[15].

Aside from mercury derivatives, which in the case of thiophenes are too numerous to mention**, polymetallic derivatives where the metal is other than lithium or magnesium are not common. To our knowledge only one other polyhaloaryl dicopper compound (1,4-dicoppertetrafluorobenzene)[17b] has been prepared, although attempts to prepare p-LiC_6Cl_4Cu-p[18] may very incidentally have resulted in a similar compound.

We report here the preparation of 2,5-dimetallodichlorothiophenes where the

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* A similar observation has been made by Rausch and co-workers; M. D. Rausch private communication. See, also, ref. 28.

** For a comprehensive survey on these, and thiophenes in general, see ref. 16.

metal is lithium, or copper. These compounds have been caused to react with chlorosilanes, acetyl chloride, allyl bromide and iodine to give the expected derivatives.

RESULTS AND DISCUSSION

Our previous attempts to prepare 2,5-dilithiodichlorothiophene in THF via n-BuLi and tetrachlorothiophene[2] resulted in a mixture, one of the components of which was tentatively identified as the dilithio compound, the other being trichloro-2-thienyllithium. Even a four-fold excess of n-BuLi was insufficient to form a pure dilithio derivative, although the ratio (di/mono) was increased by the excess, indicating an equilibrium of the kind (1):

(1)

In ether, the reaction of tetrachlorothiophene and n-BuLi has been found to give 2,5-dilithiodichlorothiophene in good yield as a very slightly soluble solid*. A large excess of n-BuLi was not required. The precipitation of the solid dilithio derivative may be in part responsible for the facile preparation since this would drive an equilibrium like (1) to the right.

The dilithio derivative reacts exothermally with chlorosilanes and carbon dioxide to give the expected silanes and acid, respectively. The reactions are considerably more exothermic than the reactions of trichloro-2-thienyllithium. The halogen–metal exchange reaction (eqn. 2) of 2,5-dilithiodichlorothiophene and tetrachlorothiophene gives a mixture in favor of trichloro-2-thienyllithium (Table 1). Possibly an equilibrium may be involved.

TABLE 1

VPC ANALYSIS (SUBSEQUENT TO HYDROLYSIS) AFTER THE ADDITION OF C_4Cl_4S TO 2,5-$Li_2C_4Cl_2S$[a]

Time	*C_4Cl_4S (relative area)*	*2,3,4-C_4Cl_3HS (relative area)*	*3,4-$C_4Cl_2H_2S$ (relative area)*
10 min	24	6	70
20 min	24	7	70
30 min	24	6	70
1 h	24	6	70
3 h	23	8	69
12 h	20	16	64
60 h	11	41	48
78 h	8	49	43

[a] See the experimental section for details.

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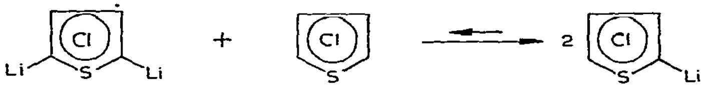
* *Warning.* This solid was isolated and dried to give a freeflowing white powder which decomposes slowly at 115–120°. It can react explosively with moisture and oxygen. When heated rapidly, the decomposition is explosive. The compound is apparently not sensitive to shock.


(2)

The yields of dichlorothiophene derivatives from the dilithio compound were in general comparable to those of trichloro-2-thienyllithium[2].

Previous studies[19] had shown that despite its seemingly greater reactivity, 2,5-dilithiodichlorothiophene did not cause ketone formation via carbonation[20,21] even under rather drastic conditions. This may be due to steric effects although electronic considerations cannot be ruled out.

The 2,5-dilithiodichlorothiophene reacts with copper(I) halides to yield the 2,5-dicopper(I)dichlorothiophene* and, much less successfully, with cadmium chloride to give the corresponding bis(chlorocadmium) derivative.

The dicopper compound which separates from solution as a heavy insoluble oil, reacts with acetyl chloride, iodine and with allyl bromide to give 2,5-diacetyldichlorothiophene, 2,5-diiododichlorothiophene, and 2,5-diallyldichlorothiophene, respectively, in good yield. In accordance with the expected lesser reactivity of the copper compound (as compared to the lithium derivative), it did not react with an excess of chlorotrimethylsilane after 6 h at room temperature. Although the heavy oil, which was apparently a complex of THF with 2,5-dicopper(I)dichlorothiophene, reacts violently with acetyl chloride in the absence of solvent, the dicopper reagent did not undergo a halogen–metal exchange reaction with tetrachlorothiophene in THF even after 2 days at 50°.

The reaction of the copper compound with iodine resulted in the main product (2,5-diiododichlorothiophene) and, in addition, traces of a compound tentatively identified as tetraiodothiophene. Disproportionation reactions involving iodothiophenes in which these derivatives react to yield all possible redistribution products are known[23]. Such reactions with mixed iodo–chloro derivatives are not described. The tetraiodo compound formed is probably not evidence of a tetracopper derivative since there is no indication of such a compound in either the reaction with acetyl chloride or VPC examination of hydrolyzed portions of the reaction mixture. The presence of copper(I) halides as well as lithium salts in the mixture may have a catalytic effect on any disproportionation which may occur. That the redistribution reaction is not extensive is evidenced by the high yield of 2,5-diiododichlorothiophene (Table 2).

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen in a three-necked flask equipped with a stirrer and a dropping funnel. Glassware was dried at 120°, assembled while hot and flushed with dry nitrogen prior to introducing the reagents. Commercial solutions of n-butyllithium in hexane (Foote Mineral Co.) and organochlorosilanes (Union Carbide Corp. and Dow-Corning Corp.) were used as supplied. Copper(I) iodide was obtained from Alfa Inorganics and was used without further purification. Copper(I) chloride was a commercial sample which was further

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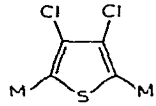
* For the sake of simplicity, the copper compounds will be referred to as simple organometallics although it is known that they probably exist as complexes[22] or cluster compounds (see ref. 29).

TABLE 2

REACTION OF THE 2,5-DIMETALLODICHLOROTHIOPHENES WITH VARIOUS DERIVATIZING REAGENTS

M[a]	*Scale (Mole)*	*Derivatizing reagent*	*Product*	*Yield (Recryst. solvent)*	*M.p. (°C) or B.p. (°C/mmHg)*
Li	0.025–0.05	CO_2	2-HOOC-C_4Cl_2S-COOH-5	87–96% (acetone/H_2O)	330–331[b]
Li	0.05	Me_3SiCl	2,5-$(Me_3Si)_2C_4Cl_2S$[c]	11.9 g, 80%	79/0.07
Li	0.05	Me_2HSiCl	2,5-$(Me_2HSi)_2C_4Cl_2S$[d]	10.1 g, 82%	92/1.0
Li	0.05	Me_2SiCl_2	Polymeric material	5.4 g, 51%[e]	230–250
Cu	(0.025)	CH_2=$CHCH_2Br$	2,5$(CH_2$=$CHCH_2)_2C_4Cl_2S$[f]	3.9 g, 66%	77–78/0.3
Cu	0.05	MeCOCl	2,5-$(MeCO)_2C_4Cl_2S$[g]	60–64% (xylene/acetone)	172.5–173
Cu	0.05	I_2	2,5-$I_2C_4Cl_2S$	10.5 g, 52%	102–102.5[h]
CdCl	0.05	MeCOCl	2,5-$(MeCO)_2C_4Cl_2S$	(Petr. ether) 8%[i]	
CdCl	0.05	I_2	[j]	18.1 g	98–185

[a] M in



[b] Cited[26]: 314–315°. Neutralization equivalent. Found: 121.3, 121.6. Calcd. for $C_6Cl_2H_2O_4S$: 120.5. Several reactions yielded 98–99% of the acid, m.p. 329–330°, which was not further purified.

[c] *Analysis.* Found: C, 40.00; H, 6.24; Si, 19.10. $C_{10}Cl_2H_{18}SSi_2$ calcd.: C, 40.39; H, 6.24; Si, 18.89%.

[d] *Analysis.* Found: C, 35.5; H, 5.38; Si, 21.61. $C_8Cl_2H_{14}SSi_2$ calcd.: C, 35.68; H, 5.24; Si, 20.86%.

[e] Yield based on $(C_4Cl_2SSiMe_2)_n$ type of polymer. The material was insoluble in the usual solvents (*e.g.*, THF, ether, CCl_4 $CHCl_3$, C_6H_6, petr. ether, C_2H_5OH, dioxane).

[f] *Analysis.* Found: Cl, 30.29. $C_{10}Cl_2H_{10}S$ calcd.: Cl, 30.41%.

[g] The effect on the yield of using CuI *vs.* CuCl in the preparation of the copper compound was negligible. *Analysis.* Found Cl, 29.97. $C_8Cl_2H_6O_2S$ calcd.: Cl, 29.90%.

[h] Cited[27]: 106°.

[i] Yield was determined by VPC. The retention time was compared with that of an authentic sample (Table 3). See footnoteg

[j] No pure products were isolated. The material appeared to be polymeric. It was insoluble in most of the usual solvents

purified[24] prior to use. Ethereal solvents and THF were distilled from sodium benzophenone ketyl. All other solvents were used without further purification.

VPC analyses were made using a 4′ × 1/4″ column of Silicone Gum Rubber (15% on Chromosorb W).

Preparation of 2,5-*dilithiodichlorothiophene*

To a 500 ml reaction flask was added 100 ml dry ether and 11.06 g (0.05 mole) of tetrachlorothiophene. The mixture was cooled to 5–10° and n-BuLi (0.105 mole, 5% excess) was added during 15–20 min. The reaction mixture first became dark-yellow to pale-straw in color. After the n-BuLi had been added, a white precipitate began to form (2,5-dilithiodichlorothiophene). The cooling bath was removed at this time and the mixture stirred for 1/2 h and then derivatized. Alternatively, the cooling bath may be left on and the mixture stirred for 1.5–2 h prior to derivatization. VPC analysis of an hydrolyzed aliquot showed a predominant peak (>99% of the total area) of shorter retention time than either C_4Cl_4S or 2-C_4Cl_3HS. This was subsequently shown to be 3,4-$C_4Cl_2H_2S$.

The dilithium compound (0.05 mole) prepared as above was hydrolyzed (at $-10°$) with 100 ml of 3*N* HCl. The organic layer was separated and the solvent evaporated to leave a brown oil. Distillation of this oil gave 5.1 g (68%) of 3,4-dichlorothiophene, b.p. 92°/43 mm, n_D^{20} 1.5720 (cited[16] 1.5760). The ^1H NMR spectrum showed only a singlet at τ 2.92. (Note: of the dichlorothiophenes, only the 3,4- and 2,5-dichlorothiophene (n_D^{20} 1.5608)[16] will show a singlet in the NMR. Since one of the lithium atoms is known[2] to be in the 2-position, the isomer must be 3,4-dichlorothiophene).

To 2,5-dilithiodichlorothiophene (0.05 mole) prepared as above was added tetrachlorothiophene (5.53 g, 0.025 mole) and the mixture stirred at 0°. The reaction was monitored by VPC (subsequent to hydrolysis). See Table 1 for the results.

Preparation of 2,5-dicopper(I)dichlorothiophene

2,5-Dilithiodichlorothiophene (0.05 mole) was prepared in ether and then cooled to $-70°$ (Dry-Ice/acetone). THF (150–200 ml) was slowly added followed immediately by 0.10 mole of the copper(I) halide (CuCl or CuI). The mixture was then stirred while warming to ca. 0° during 3–5 h. The reaction can be monitored by periodically checking with Color Test I[25]. There was apparently little or no reaction until the temperature had reached about $-20°$ (as indicated by the color of the mixture and Color Test I). When the formation of the copper compound was complete, the reaction mixture consisted of a dark brown oil suspended in a light brown solution. The compound was then derivatized. An alternative procedure was to cool the 2,5-dilithiodichlorothiophene to ca. $-70°$ and remove the ether by filtration. THF was then added and the procedure was as above. The dilithium reagent is virtually insoluble in the ether/hexane mixture and very little is lost by this method. The dicopper derivative is somewhat more soluble in the THF alone than in ether/hexane/THF.

Preparation of 2,5-bis(chlorocadmium)dichlorothiophene

2,5-Dilithiodichlorothiophene (0.05 mole) was prepared in the usual way. To this was added 18.4 g (0.1 mole) of $CdCl_2$ and the mixture stirred for 48 h at room temperature at which time Color Test I was still positive. THF (100 ml) was added and the stirring continued. After 1 h, Color Test I was negative. It was subsequently discovered that THF added at the beginning of the reaction caused the reaction to be complete within 2 h. A large amount of a sticky insoluble material was noticed in the bottom of the flask. Attempts to prepare 2,5-diiododichlorothiophene and 2,5-diacetyldichlorothiophene from this compound were quite unsatisfactory. However, the following is supporting evidence for the low yield of a dicadmium compound: treatment of a small aliquot of 2,5-dilithiodichlorothiophene with excess CH_3COCl failed to yield any detectable (by VPC) 2,5-diacetyldichlorothiophene.

The various derivatives, yields and pertinent data are collected in Table 2. Some spectral data are listed in Table 3.

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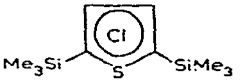
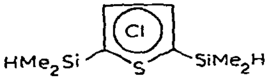
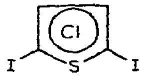
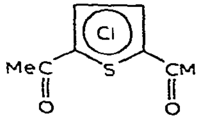
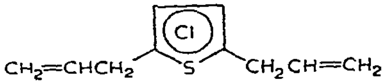
TABLE 3

SPECTRAL DATA OF COMPOUNDS DERIVED FROM 2,5-DIMETALLO-3,4-DICHLOROTHIOPHENES

Compound	*IR* (cm^{-1})[a]	*NMR*[b] (*ppm*)	*Mass Spec.* (*m/e*)[c]
	2950 m, 2890 (sh), (C–H); 1502 m, 1410 s, 1308 s, 1278 w, (3,4-C_4Cl_2S); 1250 s, 842 vs, 760 (sh), ($SiMe_3$).	Singlet 9.62 (Si–CH_3)	$(M)^+$; 296, 298, 300 (Calcd.: 297.4) $(M-CH_3)^+$; 281, 283, 285 (Calcd.: 282.4)
	2970 m, 2900 (sh), (C–H); 2140 s, (Si–H); 1470 w, 1395 m, 1300 s, 1280 s, (3,4-C_4Cl_2S); 1250 s, 840 vs, 768 s ($SiMe_2$).	Multiplet 5.48 (Si–H). Doublet 9.58, $J=3.7$ Hz (CH_3). (Integration Found: 0.96/6.0. Calcd.: 1.0/6.0)	$(M)^+$; 268, 270, 272 (Calcd.: 269.3) $(M-CH_3)^+$; 253, 255, 257 (Calcd.: 254.3)
			$(M)^+$; 404, 406, 408 (Calcd.: 404.9) $(M-I\cdot)^+$; 277, 279, 281 (Calcd.: 277.9) $(M-2I\cdot)^+$; 150, 152, 154 (Calcd.: 150.9)
 [d]	2950 m, 2890 (sh) (C–H); 1645 s (C=O); 1500 w, (CH_3)	Singlet 7.28 $(-\underset{\underset{O}{\parallel}}{C}-CH_3)$	$(M)^+$; 236, 238, 240 (Calcd.: 237.1) $(M-CH_3)^+$; 221, 223, 225 (Calcd.: 222.1)
	3100 w, 2990 w, 2900 w, (C–H); 1642 m, (C=C); 1545 w, 1428 m, 1333 s, 1280 w, (3,4-C_4Cl_2S)	Typical allyl pattern showing multiplets at 4.15, 4.92 and 6.55. (Integration. Found: 1.0/2.0/2.0. Calcd.: 1.0/2.0/2.0)	$(M)^+$; 232, 234, 236 (Calcd.: 233.2) $(M-CH_2CH\cdot)^+$; 205, 207, 209 (Calcd.: 206.2) $(M-Cl\cdot)^+$; 197, 199 (Calcd.: 197.7)

[a] Spectra were taken of neat liquids on NaCl plates using a Perkin–Elmer Model 21 infrared spectrophotometer.

[b] All NMR data were determined relative to TMS in CCl_4 solution on a Varian A-60 NMR Spectrometer.

[c] Calculated values are based on Cl = 35.45. The isotopic pattern and intensities were as expected for compounds containing two chlorine atoms.

[d] The IR spectrum was determined as a fluorolube mull.

tract No. F33615-69-C-1046 monitored by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. The authors are grateful to Dr. Victor Mark of the Hooker Chemical Corp. for some of the tetrachlorothiophene.

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