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Chlorinated 2,3′-Dithienyls. The By-products Formed in the Coupling of Thiophene with Sulfuryl Chloride and Iron Powder[1,2]

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The reaction of thiophene with sulfuryl chloride has been known to give chlorothiophenes. In the presence of iron powder or a Friedel-Crafts-type catalyst, however, the reaction affords the chlorinated 2,2′-dithienyls (**1b**—**e**) as the main product.[2] In addition to **1b**—**e**, the product has been shown by vapor-phase chromatography (vpc) to contain 10—20% of unidentified materials, in which one component (**2c**) predominates. Although there have been several papers concerning the coupling of aromatic nuclei, little has been known about that of thiophene nuclei. The present work was undertaken in order to isolate and identify the by-products and to obtain information concerning the coupling of thiophene nuclei.

The crystalline product was sublimed repeatedly under reduced pressure, and the more volatile part was submitted to fractional recrystallization from petroleum ether. Compound **2c** (mp 53—54 °C), isolated from the more soluble part, seems to be 2′,5-dichloro-2,3′-dithienyl, judging from its UV and NMR spectral data and elemental analysis. Thus, the observed maximum (298 nm) of the UV absorption is a little lower than that of 2,2′-dithienyl (**1a**) itself and is rather similar to that of 2,3′-dithienyl (**2a**), while in the NMR spectrum, the coupling constants of two sets of double-doublets (J=3.9 and 5.9 Hz) in the ring-proton region and the relative peak intensities indicate the presence of both one 2,3-di-, and one 2,5-disubstituted thiophene rings in **2c**.[3] The assignment was finally confirmed by comparison with the authentic sample prepared by the chlorination of **2a**. The presence of 2′-chloro- (**2b**), and 2′,3,5-trichloro-2,3′-dithienyls (**2d**) as minor products was also detected by vpc. Some representative results of the coupling reaction are shown in Table 1. It is worth noting that considerable amounts of 2,3′-dithienyl derivatives are formed in the coupling of the thiophene nuclei, the

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[1] Acid-catalyzed Oligomerization of Thiophene Nuclei. II.

[2] Part I: T. Sone, K. Sakai, and K. Kuroda, This Bulletin, **43**, 1411 (1970).

[3] For the UV and NMR spectral data concerned, see the previous paper and the references cited therein.

Table 1. Reaction of thiophene with sulfuryl chloride and iron powder[a)]

Mole ratio Thiophene/ SO_2Cl_2	Fe(g)	Chlorinated dithienyls, yield, mol %[b)]						
		1b	**1c**	**1d**	**1e**	**2b**	**2c**	**2d**
1:1	0.3	trace	10	16	1	trace	7	trace
1:1	0.3 CCl_4 (20 ml)	trace	7	9	0.5	trace	4	

a) Reaction condition: thiophene 0.125 mol; 3 hr at room temperature.

b) Based on thiophene used.

Table 2. Chlorination of dithienyls with sulfuryl chloride[a)]

Mole ratio **1a** or **2a**/ SO_2Cl_2	**1a** or **2a**	Chlorinated dithienyls, yield, mol %[b,c)]			
		1b or **2b**	**1c** or **2c**	**1d** or **2d**	**1e**
2,2′-Dithienyls (**1**)					
1 : 1	20 (24)	61 (57)	11 (14)	(3)	
1 : 2		47 (28)	35 (34)	4 (7)	
1 : 3		24 (4)	65 (40)	7 (11)	
1 : 10			69 (20)	22 (32)	1.5> (4)
2,3′-Dithienyls (**2**)					
1 : 1	27 (22)	55 (42)	7 (12)		
1 : 2		53 (10)	41 (36)	(9)	d)
1 : 3			88 (35)	7 (14)	d)
1 : 10			34 (21)	47 (22)	d)

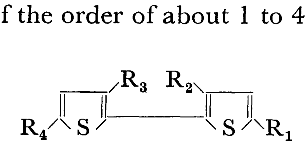
a) Reaction conditions: Dithienyl, 5 mmol in carbon tetrachloride (5 ml); 30 min at room temperature and additional 30 min at the boiling point of the reaction mixture.

b) Based on the dithienyl used.

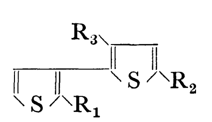
c) Figures in the parentheses represent the yields obtained by the addition of ferric chloride (0.2 g, 1.233 mmol) in the reaction. In the presence of ferric chloride, the reactions are usually accompanied with the formation of a resinous material.

d) Besides **2b**—**d**, a small amount of higher chlorinated products were formed, when the reaction was carried out in the presence of ferric chloride.

proportion of 2,3′- to 2,2′-dithienyl derivatives being of the order of about 1 to 4.



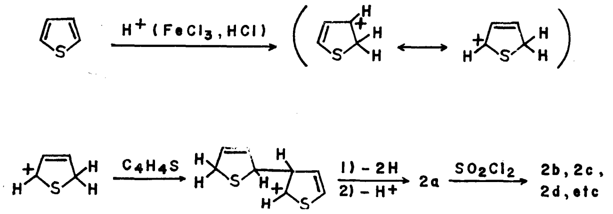
1a: $R_1=R_2=R_3=R_4=H$
1b: $R_1=Cl$, $R_2=R_3=R_4=H$
1c: $R_1=R_4=Cl$, $R_2=R_3=H$
1d: $R_1=R_2=R_4=Cl$, $R_3=H$
1e: $R_1=R_2=R_3=R_4=Cl$



2a: $R_1=R_2=R_3=H$
2b: $R_1=Cl$, $R_2=R_3=H$
2c: $R_1=R_2=Cl$, $R_3=H$
2d: $R_1=R_2=R_3=Cl$

In order to prepare authentic samples and to seek explanation for the formation of the chlorinated dithienyls, a brief study of the chlorination of **1a** and **2a** with sulfuryl chloride was carried out (Table 2); the chlorination occurs preferentially at the 5-position of **1a** and the 2′-position of **2a**, and successively at the 5′-, the 3-, and the 3′-positions for **1a**, and at the 5-, and the 3-positions for **2a**. The results are of interest, as only a little has been known concerning the substitution reactions of dithienyls, particularly those of **2a**. The reaction is promoted by the presence of ferric chloride to give the polychlorinated dithienyls in a higher proportion and a resinous material to some extent; the normal course of the chlorination is essentially unaltered.

In the previous paper, it was suggested that **1b**—**e** were formed by the coupling of the thiophene nuclei *via* a cationic mechanism, the reaction being initiated by the protonation of thiophene, followed by the chlorination of the resulting **1a**.[4)] Taking into account the appreciable 3-substitution in certain electrophilic alkylations of thiophene and the results of the chlorination of **2a**, the formation of **2b**—**d** may be explained by the same mechanism, as is shown in Scheme 1.



Experimental[5)]

Isolation of 2′,5-Dichloro-2,3′-dithienyl (**2c**) *from the Coupling Product.* The crystalline coupling product[2)] (60 g) was sublimed repeatedly under reduced pressure (110—130 °C/ 2—4 mmHg; the more volatile part (15 g) was then triturated with cold petroleum ether. The solvent was evaporated from the washings, and the residue was treated several times in a similar manner and finally recrystallized from the same solvent to give crude **2c** (2 g), which was subsequently purified by column chromatography on silica gel, using petroleum ether as the eluant; colorless needles, mp 53—54 °C. UV (MeOH) λ_{max} nm (log ε): 298 (4.25), 249 (4.10). NMR (Me_2CO) δ: 7.06 (d, J=3.9 Hz, 4-H), 7.38 (d, J=3.9 Hz, 3-H), 7.30 (d, J=5.9 Hz, 4′-H), 7.47 (d, J=5.9 Hz, 5′-H). Found: C, 40.92; H, 2.10%. Calcd for $C_8H_4Cl_2S_2$: C, 40.85; H, 1.71%.

Chlorination of 2,2′- (**1a**) *and 2,3′-Dithienyls* (**2a**). *a) General Procedure.* Sulfuryl chloride was added to a stirred solution of the dithienyl (0.84 g, 5 mmol) in carbon

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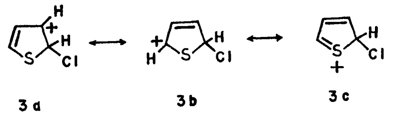
[4)] Another possibility is the intermediary formation of the carbonium ions, **3a**—**c**, from thiophene through a reaction with the chlorinium ion, which attacks the 2-position of a thiophene molecule, followed by dehydrogenation and by the loss of a proton to yield **1b** and **2b**. This mechanism was suggested by the referee.



3a 3b 3c

[5)] All the melting and boiling points are uncorrected. The UV spectra were obtained on a Hitachi EPU-2A spectrophotometer, and the NMR spectra, on a Hitachi R-20A spectrometer, at 60 MHz, using tetramethylsilane as the internal reference.

tetrachloride (5 ml), and then the reaction mixture was stirred for 30 min. After being stirred for an additional 30 min at the boiling point, the mixture was poured into ice water (30 g) and extracted with carbon tetrachloride (30 ml). The organic layer was washed with a dilute sodium bicarbonate solution and then with water, and dried. The solvent was evaporated, and the residue was analyzed by vpc as has been described previously.[2] The reactions in the presence of anhydrous ferric chloride (0.2 g, 1.233 mmol) were carried out in a similar manner. The results are given in Table 2.

b) 2′,5-Dichloro-2,3′-dithienyl (2c). The product (2.0 g) obtained by the reaction of **2a** (1.7 g, 0.01 mol) with two molar equivalents of sulfuryl chloride (2.7 g) was recrystallized twice from light petroleum ether to give **2c** (mp 53—54 °C, 0.6 g). This compound was proved to be identical with the **2c** isolated from the coupling product by a comparison of their IR and UV spectra and by a mixed-melting-point determination.

c) 2′-Chloro-2,3′-dithienyl (2b). A solution of sodium acetate trihydrate (67 g) in water (100 ml) was added to the mixture (5 g) of **2b** and **2c** in ethanol (380 ml) which had been obtained by the reaction of **2a** with two molar equivalents of sulfuryl chloride; to the resulting solution was then added a saturated solution of mercuric chloride (200 ml). The reaction mixture was allowed to stand for 3 days, after which the precipitates (3.4 g) were filtered off and recrystallized from chloroform to yield the chloromercury derivative of **2b** (2.3 g, mp 210—250 °C). The mercury derivative was heated with a mixture of hydrochloric acid (15 ml) and water (30 ml) on a water bath for 30 min, and the oil (1.0 g) thus separated out was extracted with chloroform. The extract was washed with a sodium bicarbonate solution and then with water, and dried. The solvent was evaporated and the residue distilled to afford **2b** (0.8 g); bp 103—104 °C/4 mmHg, n_D^{20} 1.6625. UV (MeOH) λ_{max} nm (log ε): 287 (4.14), 244 (4.10). NMR (Me_2CO) δ: 7.13 (q, J=3.7 Hz, J=5.0 Hz, 4-H), 7.51 (q, J=5.0 Hz, J=1.1 Hz, 5-H), 7.53 (q, J=3.7 Hz, J=1.1 Hz, 3-H), 7.31 (d, J=5.9 Hz, 4′-H), 7.42 (d, J=5.9 Hz, 5′-H).[6] Found: C, 48.06; H, 2.26%. Calcd for $C_8H_5ClS_2$: C, 47.87; H, 2.51%.

d) 2′,3,5-Trichloro-2,3′-dithienyl (2d).[7] The further chlorination of a mixture of **2b** and **2c** with a large excess of sulfuryl chloride (6 times by weight) in carbon tetrachloride gave **2d**; colorless crystals; mp 77—78 °C (from petroleum ether). UV (MeOH) λ_{max} nm (log ε): 278 (4.05), 249 (4.10). NMR (Me_2CO-d_6) δ: 7.11 (s, 4-H), 7.21 (d, J=5.7 Hz, 4′-H), 7.50 (d, J=5.7 Hz, 5′-H). Found: C, 35.87; H, 0.82%. Calcd for $C_4H_3Cl_3S_2$: C, 35.63; H, 1.12%.

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[6] The spectrum was analyzed by Professor Kensuke Takahashi (Nagoya Institute of Technology), to whom the authors are indebted.

[7] It is interesting to note that, unlike the chlorination, the tribromination of **2a** with *N*-bromosuccinimide has been reported to give the 2′,5,5′-trisubstituted derivative.[8]

[8] R. M. Kellogg, A. P. Schaap, and H. Wynberg, *J. Org. Chem.*, **34**, 343 (1969).