BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1411—1415 (1970)

Chlorinative Coupling of Thiophene by the Action of Sulfuryl Chloride and Iron Powder[*1]

Tyo SONE, Koji SAKAI and Kimio KURODA

Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa

(Received July 14, 1969)

In the presence of iron powder, thiophene reacted with sulfuryl chloride at room temperature to give a mixture of chlorinated 2,2′-dithienyls as the main product in yields of up to 42%, while the reaction without a catalyst gave chlorothiophenes. The yield of the coupling product and the chlorine content in the product increase with an increase in the molar ratio of sulfuryl chloride to thiophene. 5,5′-Dichloro-, 3,5,5′-trichloro-, and 3,3′,5,5′-tetrachloro-2,2′-dithienyls were isolated from the reaction products. The reaction was also catalysed by Friedel-Crafts-type catalysts, the efficiency of the catalysts decreasing in the order: $AlCl_3 > FeCl_3 > SnCl_4 > ZnCl_2$.

There have been several papers concerning the coupling of aromatic[1] and heteroaromatic compounds[2,3] with halogenating agents. In one of these papers, Töhl and Eberhard briefly and without structural elucidation described the forma-

---

[*1] Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

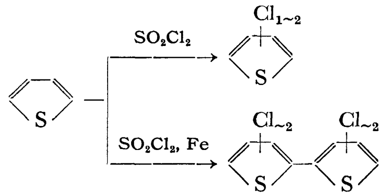
[1] K. Bowden and C. H. Reece, *J. Chem. Soc.*, **1950**, 1686.

[2] A. Töhl and O. Eberhard, *Ber.*, **26**, 2940 (1893).

[3] a) M. Kunori, *Nippon Kagaku Zasshi*, **83**, 836 (1962); b) M. Kunori, *ibid.*, **83**, 839 (1962).

tion of chlorinated 2,2′-dithienyls by the reaction of thiophene with sulfuryl chloride and aluminum chloride.[2)]

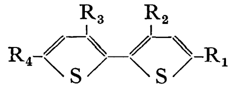
In the presence of iron powder as well as Friedel-Crafts-type catalysts, thiophene was found to react with sulfuryl chloride at room temperature to afford chlorinated 2,2′-dithienyls as the main product, while the reaction without a catalyst has been known to give 2-chloro- and 2,5-dichlorothiophene.[4)] These facts are of interest not only from mechanistic but also from preparative points of view. Certain 2,2′-dithienyl derivatives, including 5,5′-dichloro-2,2′-dithienyl (II), have been shown to have a strong nematicidal activity.[5)] Previous procedures of preparing 2,2′-dithienyls are based on the coupling of 2-halothiophene by the Ullmann or Grignard method. On the other hand, the present method may provide a convenient, one-step synthesis of those compounds.



The object of the present work is to ascertain the reaction conditions which favor the formation of the coupled products, to isolate the products, and to identify their structures.

Results and Discussion

The reaction of thiophene with sulfuryl chloride and iron powder afforded a crystalline product along with a small amount of liquid chlorothiophenes (less than 10%) and a polymeric material. The crystalline product melted over a rather wide temperature range (60—100°C); it has been suggested that it has a dithienyl structure on the basis of UV spectral and molecular-weight determination. In addition, the product gave a positive test for the Beilstein test. These facts indicate that the product is mainly a mixture of chlorine-substituted dithienyls, presumably chlorinated 2,2′-dithienyls. Although the separation of a pure chlorinated 2,2′-dithienyl from the others is not easy, as has been pointed out in connection with the preparation of 5-chloro-2,2′-dithienyl by the direct chlorination of 2,2′-dithienyl,[5,6)] three chlorinated 2,2′-dithienyls, *i. e.*, II, 3,5,5′-trichloro-2,2′-dithienyl (III) and 3,3′,5,5′-tetrachloro-2,2′-dithienyl (IV), could be isolated by the fractional recrystallization of the reaction mixtures.



(I): $R_1=Cl, R_2=R_3=R_4=H$
(II): $R_1=R_4=Cl, R_2=R_3=H$
(III): $R_1=R_2=R_4=Cl, R_3=H$
(IV): $R_1=R_2=R_3=R_4=Cl$
(V): $R_1=R_2=R_3=Cl, R_4=H$

The product obtained from the reaction of thiophene with a large excess of sulfuryl chloride consisted principally of tetrachloro-2,2′-dithienyl. The positional assignment of chlorine atoms was based on the NMR spectrum of the dechlorination product of the tetrachloro-2,2′-dithienyl with zinc powder in an acetic acid solution. The spectrum of the trichloro-2,2′-dithienyl thus obtained shows a singlet and two doublets with a relative intensity of 1 : 1 : 1, as is shown in Table 1. The singlet at 6.84 ppm is due to the hydrogen at the β-position of one thiophen ring, and the doublets at 7.32 ppm and 6.95 ppm correspond to two hydrogens of the other ring in the trichloro-2,2′-dithienyl, coupling constant (J=5.5 Hz) being indicative of 2,3-disubstituted thiophene.[7)] These results are in agreement with those to be expected for 3,3′,5-trichloro-2,2′-dithienyl (V), which in turn indicate that the original tetrachloro-2,2′-dithienyl is IV.

II and III were isolated from the products obtained by the reactions of thiophene with a one-half molar equivalent of sulfuryl chloride (Table 2, No. 3) and with an equimolar amount of sulfuryl chloride (Table 2, No. 4) respectively, but in low yields. II was identified by comparison with the authentic sample prepared from 2-chloro-5-iodothiophene by the Ullmann reaction. The structure of III was confirmed by means of NMR spectroscopy, as in the case of V.[7)] The UV and NMR spectral data of the chlorinated 2,2′-dithienyls are summarized in Table 1.

The effects of the molar ratio of sulfuryl chloride to thiophene and catalysts on the composition of the product were studied in some detail. The crystalline products[8)] obtained under various condi-

---

4) E. Campaigne and W. M. LeSuer, *J. Amer. Chem. Soc.*, **70**, 415 (1948).

5) J. H. Uhlenbroek and J. D. Bijloo, *Rec. Trav. Chim. Pays-Bas*, **79**, 1181 (1960).

6) W. Steinkopf, "Die Chemie des Thiophens," Steinkopf, Dresden and Leipzig (1941), p. 143.

7) S. Gronowitz, "Advances in Heterocyclic Chemistry," Vol. 1, ed. by A.R. Katritzky, Academic Press, New York (1963), p. 7. The coupling constants between two protons in disubstituted thiophenes are: J_{35}=1.25—1.70 Hz, J_{25}=3.20—3.65 Hz, J_{34}=3.45—4.35 Hz, and J_{45}=4.90—5.80 Hz.

8) The IR spectra of the crystalline products exhibit a moderate band other than those of the chlorinated 2,2′-dithienyls at about 710 cm^{-1}. It was also shown by vpc that the crystalline products usually consisted of 10—20% of unidentified materials in which one component predominated; when zinc chloride was used as the catalyst, the crystalline product, exceptionally, consisted of about 30% unidentified materials.

TABLE 1. SPECTRAL DATA OF CHLORINATED 2,2′-DITHIENYLS

Compd.	UV λ_{max}^{MeOH} mμ (log ε)*1	NMR δ*2
2,2′-dithienyl	246 (3.80), 302 (4.09)	6.84 (4-H) 7.00 (5-H) 7.02 (3-H) *3
2,3′-dithienyl	235 (3.92), 283 (4.07)*4	
I	247 (3.77), 311 (4.14)*5	
II	245 (3.76), 317 (4.22)	6.73 (d, 3-H or 4-H) 6.80 (d, 3-H or 4-H) J=4.0 Hz
III	256 (3.75), 317sh (4.19) 326 (4.20)	6.78 (4-H) 6.83 (d, 3′-H or 4′-H) 7.02 (d, 3′-H or 4′-H) J=4.0 Hz
IV	257 (3.99), 298 sh (4.00) 309 (4.04), 325 sh (4.00) 338 sh (3.79)	6.84 (4-H)
V	257 (3.99) 303 (3.96) 313 sh (3.92), 330sh (3.67)	6.84 (4-H) 6.95 (d, 4′-H or 5′-H) 7.32 (d, 4′-H or 5′-H) J=5.5 Hz

*1 sh: shoulder
*2 Measured in carbon tetrachloride solution.
*3 K. Takahashi, private communication.
*4 H. Wynberg and A. Bantjes, *J. Org. Chem.*, **24**, 1421 (1959). Measured in ethanol solution.
*5 Data reported in Ref. 12. Measured in ethanol solution.

TABLE 2. REACTION OF THIOPHENE WITH SULFURYL CHLORIDE AND IRON POWDER
(Reaction temperature, room temperature; Reaction time, 3 hr)

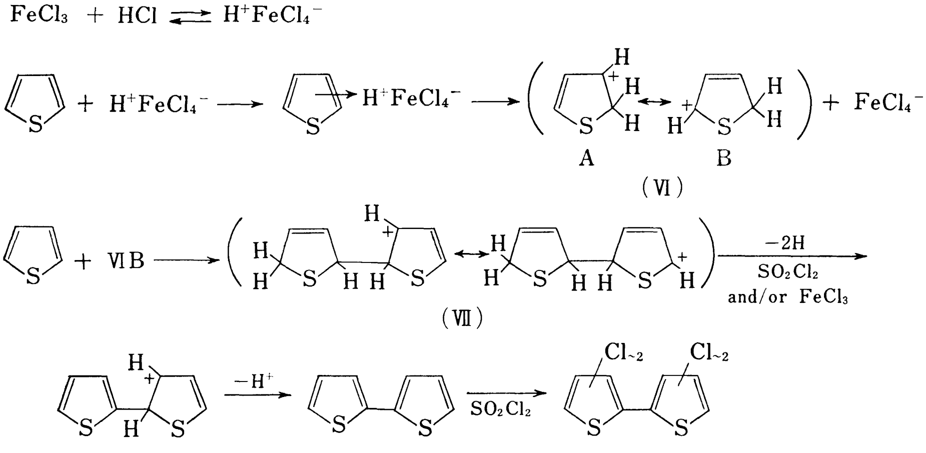
No.	Thiophene g	Mol ratio thiophene/ SO_2Cl_2	Catalyst	Chlorinated 2,2′-dithienyls Yield (Mol-%*1)			
				I	II	III	IV
1	21.0	1 : 1	none	2-chlorothiophene 2,5-dichlorothiophene		39.8% 4.7%	
2	21.0	1 : 0.1	Fe 0.5 g	0.2	2	0.2	—
3	21.0	1 : 0.5	Fe 0.5 g	trace	10	5	—
4	21.0	1 : 1	Fe 0.5 g	trace	9	13	1
5	21.0	1 : 2	Fe 0.5 g	—	2	25	11
6	10.5	1 : 5	Fe 0.5 g	—	—	—	42
7	21.0	1 : 1	Fe 5.0 g	trace	7	8	0.5
8	21.0	1 : 1	Fe 0.5 g $PhNO_2$ 20 m*l*	trace	7	12	1
9	21.0	1 : 1	Fe 0.5 g S 2 g	trace	9	14	1
10	16.8	1 : 1	$AlCl_3$ 0.45 g*2	trace	13	15	1
11	16.8	1 : 1	$FeCl_3$ 0.55 g*2	trace	11	14	1
12	16.8	1 : 1	$SnCl_4$ 0.88 g*2	trace	5	7	0.3
13	16.8	1 : 1	$ZnCl_2$ 0.46 g*2	trace	1	4	1

*1 Based on thiophene used.
*2 3.4 mmol.

tions were shown by vapor-phase chromatography (vpc) to consist mainly of a mixture of chlorinated 2,2′-dithienyls, the composition depending on the conditions employed. Table 2 shows the results. The yield of the coupling product, and at the same time the chlorine content in the product, increase with an increase in the molar ratio of sulfuryl chloride to thiophene. An increase in the amount of iron powder tends to increase the formation of the polymeric material. The presence of sulfur or nitrobenzene, which is known to retard free-radical reactions, did not essentially influence the composition of the product. The reaction was also catalyzed by Friedel-Crafts-type catalysts, the efficiency of the catalysts in the coupling reaction then decreasing in the order: $AlCl_3 > FeCl_3 > SnCl_4 > ZnCl_2$.[9] This

---

[9] The use of zinc chloride as a catalyst particularly tends to increase the chlorine content in the product; the reason for this is not clear.



Scheme 1

order is substantially in agreement with that observed in the Friedel-Crafts reaction.[10] These results suggest that the chlorinative coupling of thiophene proceeds *via* an ionic mechanism.

Attempts to isolate 5-chloro-2,2′-dithienyl (I),[11] the presence of which was revealed by vpc, and the crystalline products other than I, II, III, and IV from the reaction mixtures were unsuccessful.

When another chlorinating agent, such as thionyl chloride or sulfur chloride, was used in place of sulfuryl chloride, not coupling but polymerization occurred.[13] The reaction of thiophene with bromine in the presence of iron powder gave only bromothiophenes. 2-Chlorothiophene and 2-methylthiophene, on the other hand, were merely chlorinated at the 5-position in the reaction with sulfuryl chloride and iron powder.

From the facts mentioned above, the following reaction path seems to be most probable for the chlorinative coupling of thiophene with sulfuryl chloride and iron powder (Scheme 1): The first step in the process is the protonation of thiophene by the hydrogen chloride and ferric chloride which were produced during the reaction, thus forming an ionic complex (VI) analogous to the Friedel-Crafts complex. The second step is the attack of the more stable cation, VIB, on the 2-position of a thiophene molecule, followed by the dehydrogenation of the so-formed carbonium ion intermediate (VII) with sulfuryl chloride and/or ferric chloride and then by the loss of a proton to yield 2,2′-dithienyl, although the stage at which dehydrogenation takes place is not yet clear. The chlorination of the resulting dithienyl produces chlorinated dithienyls. The repetition of the process will give polythienyls. In fact, a small amount of a polymeric material was formed in every run. The possibility of the formation of 2,3′-dithienyl derivatives (VIII) can not be ruled out, but VIII could not be isolated from the reaction mixtures. The reason why coupling does not take place with 2-chlorothiophene and with 2-methylthiophene may be expalined as follows. 2-Chlorothiophene is not basic enough to be protonated in the system, and even if it were, it is not susceptible to the attack of the so-formed cation analogous to VI in the next step. On the other hand, 2-methylthiophene is so reactive that chlorination occurs in preference to coupling.

Experimental[14]

Reaction of Thiophene with Sulfuryl Chloride in the Presence of Iron Powder. General Procedure. Sulfuryl chloride (34 g, 0.25 mol) was added to a stirred mixture of thiophene (21 g, 0.25 mol) and commercially-obtained reduced iron powder (0.5 g) at room temperature. Within several minutes the mixture darkened and sulfur dioxide and hydrogen chloride

---

[10] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York (1961), p. 651.

[11] The authentic sample was prepared according to the method described in the literature.[12]

[12] R. F. Curtis and G. T. Phillips, *J. Chem. Soc.*, **1965**, 5134.

[13] Recently, Fujisawa *et al.* found that some aromatic compounds such as anisole reacted with sulfur chloride or sulfur dichloride in the presence of iron powder to give the corresponding diaryl sulfides in fair yields. T. Fujisawa, N. Kikuchi and G. Tsuchihashi, Preprints for the 21st Annual Meeting of the Chemical Society of Japan (April, 1968), pp. 1572, 1573.

[14] All the melting points and boiling points are uncorrected. The infrared spectra were obtained on a Hitachi EPI-S2 spectrophotometer, and the ultraviolet spectra, on a Hitachi EPU-2A spectrophotometer. The NMR spectra were recorded with a Varian Associates A-60 spectrometer in carbon tetrachloride at 60 MHz, using tetramethylsilane as the internal reference. The vpc analyses were carried out on a Hitachi K23F instrument.

were evolved, but the temperature remained almost unchanged. After three hours chloroform (60 m*l*) and then water (100 m*l*) were stirred into the deep purple reaction mixture; when the mixture was stirred for an additional 10 min, the mixture turned brown. A small amount of the brown precipitate (0.5 g) was filtered and washed with chloroform. The chloroform layer was washed with water, a 5% sodium bicarbonate solution, and again with water, and then dried (Na_2SO_4). After the solvent and the unreacted thiophene (4.5 g, analyzed by vpc) had been removed, the residue was distilled under reduced pressure to give chlorothiophenes (2.4 g, bp 25—55°C/56 mmHg). The residual mass (12.2 g) was sublimed twice under reduced pressure (2—4 mmHg) at about 140°C; pale yellow crystals (8.7 g, mp 54—87°C) were thus separated from the tarry material.

The data for the various run are given in Table 2.

5,5′-Dichloro-2,2′-dithienyl (II). *a) Isolation of II from the Coupling Products.* II was isolated from the reaction mixture which had been obtained by the reaction of thiophene with a one-half molar equivalent of sulfuryl chloride (Table 2, No. 3) by fractional recrystallization from methanol; colorless leaflets; mp 107.5—109°C (lit, 109—110°C,[2] 109°C[5]).

Found: C, 41.16; H, 2.03%. Calcd for $C_8H_4Cl_2S_2$: C, 40.85; H, 1.71%.

b) Ullmann Reaction of 2-Chloro-5-iodothiophene (IX). The procedure was a modification of the method used for the preparation of 2-iodothiophene from thiophene.[15] Nitric acid (*d* 1.42; 20.6 g) was added to a stirred mixture of 2-chlorothiophene (20 g) and pulverized iodine (19.6 g) over a period of about 2 hr. During the addition, the temperature of the reaction mixture remained at 25—30°C and brown nitrogen oxides were evolved. After the addition was complete, the mixture was heated at 40—45°C for 1 hr and then at 80°C for 1 hr, after which it was treated as has been described for 2-iodothiophene. The yield was 35.5 g (86.6%); bp 94—97°C/14 mmHg (lit, 95—96°C/14 mmHg[16]).

A mixture of IX (20 g) and copper-bronze (Cu 80%, 20 g) was heated with stirring at 210—215°C for 2 hr. The reaction mixture was then cooled and carefully extracted with chloroform (100 m*l*). The solvent was removed from the extract to leave a solid material, the recrystallization of which from methanol (300 m*l*) afforded almost pure II (4.8 g, mp 108—108.5°C). The concentration of the filtrate gave an additional crop (1.0 g, mp 106—107°C) and an oily material which was assumed to be recovered IX. The total yield of II was 5.8 g (60.3%). The sublimation of the crude product under reduced pressure raised the melting point to 108—109°C. This compound was proved to be identical with the II isolated from the coupling product by a comparison of their IR and NMR spectra and by a mixed-melting-point determination.

3,5,5′-Trichloro-2,2′-dithienyl (III). III was isolated from the product which had been obtained by the reaction of thiophene with an equimolar amount of sulfuryl chloride (Table 2, No. 4) by the repeated recrystallization from methanol: mp 102—103°C (lit, 103°C[2]).

Found: C, 35.36; H, 1.11%. Calcd for $C_8H_3Cl_3S_2$: C, 35.63; H, 1.12%.

3,3′,5,5′-Tetrachloro-2,2′-dithienyl (IV). The product obtained by the reaction of thiophene (10.5 g, 0.125 mol) with five molar equivalents of sulfuryl chloride (84.5 g, 0.625 mol) was sublimed at 2—4 mmHg and at 140°C; the sublimate (9.2 g, mp 118—126°C) was then recrystallized from chloroform (160 m*l*) to give almost pure IV (5.7 g) as colorless needles; mp 127—128°C (lit, 126.5—127°C[17]) (Table 2, No. 6).

Found: C, 31.21; H, 0.83%. Calcd for $C_8H_2Cl_4S_2$: C, 30.99; H, 0.65%.

The further chlorination of a mixture of the chlorodithienyls with excess sulfuryl chloride in carbon tetrachloride at the boiling temperature of the solvent also gave IV, along with a small amount of a resinous material.

Dechlorination of IV. A mixture of IV (0.62 g), zinc dust (2.5 g), acetic acid (20 m*l*), and water (10 m*l*) was gently refluxed for 30 hr. The reaction mixture was filtered while hot, and the solid material was washed with hot acetic acid (10 m*l*). The combined filtrates were cooled to room temperature, and the resultant crystals, which consisted of zinc acetate and recovered IV (0.25 g, mp 124—127°C), were filtered off. To this filtrate, water (100 m*l*) was added to give crystals (0.19 g, mp 52—56°C); the recrystallization of these crystals from methanol yielded 3,3′,5-trichloro-2,2′-dithienyl (V) as colorless needles; mp 56—57°C.

Found: C, 35.48; H, 0.71%. Calcd for $C_8H_3Cl_3S_2$: C, 35.63; H, 1.12%.

Vapor-phase Chromatographic Analysis. Vpc analyses were performed on a stainless steel column packed with 10% Silicone DC 44M on Chromosorb WAW (Gasukuro Kogyo Co., Ltd.; 60—80 mesh; 3 mmϕ × 1 m). The column temperature was programmed from 150° to 200°C at 5°C/min; the flow rate of nitrogen gas was 8 m*l*/min. Biphenyl was used as the internal standard.

The authors wish to express their gratitude to Professor Emeritus Yasuo Matsuki of Tohoku University for his continued interest in and support of this work. Thanks are also due to Mr. Fusaji Shoji for his help in many respects.

---

[15] H. Y. Lew and C. R. Noller, "Organic Syntheses," Coll. Vol. IV, p. 545 (1963).

[16] W. Steinkopf and W. Köhler, *Ann.*, **532**, 250 (1937).

[17] O. Eberhard, *Ber.*, **28**, 2385 (1895)