  Bull. Chem. Soc. Jpn., 59, 83—87 (1986)

A Novel Friedel-Crafts Type Reaction of 2-Chlorothiophene with Some Active Aromatic Compounds[1)]

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(Received June 20, 1985)

2-Chlorothiophene (**1**) was found to easily react with certain active aromatic compounds (**2**) in the presence of $AlCl_3$ under mild conditions, yielding the corresponding 2-arylthiophenes (**3**) and 5-chloro-2,2′-bithienyl (**5**) as the main products. With compounds more reactive than **1**, the formation of **3** predominated. Reactions of **1** with aryl alkyl ethers, for example, afforded the corresponding **3** in 44—83% yields in one step.

It has been generally assumed that a chlorine atom that is directly attached to a thiophene ring is inert[2)] and cannot be replaced by an aryl group under Friedel-Crafts conditions as is true for aryl chlorides that are inert.

In contrast to this fact, Ramsey et al. have reported the polymerization of chlorothiophenes by $AlCl_3$–$CuCl_2$, which involves a nuclear coupling along with the elimination of HCl.[3)] We recently found that in the presence of a cation-exchange resin, 2-chlorothiophene (**1**) reacted with anisole (**2d**) to give 2-(*p*-methoxyphenyl)thiophene (**3d**) and its derivatives, although the yield was low.[4)] We also found that $AlCl_3$ catalyzed a Friedel-Crafts reaction involving 2,5-dichloro-3-(chloromethyl)thiophene with simple benzene derivatives and unexpectedly afforded corresponding 4-aryl-3-arylmethyl-2-chlorothiophenes as the major products.[5)]

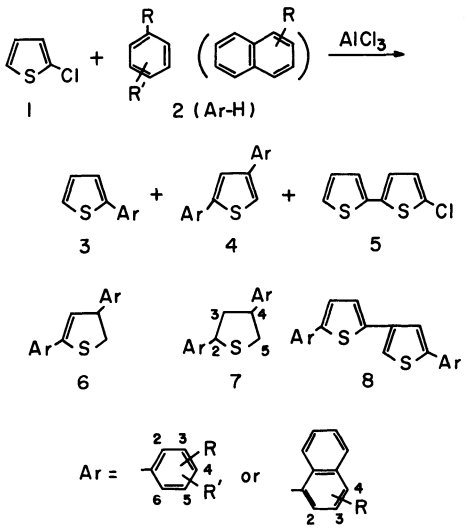
These findings suggest that chlorothiophenes can be sufficiently activated to couple with reactive aromatic compounds (**2**) under appropriate acidic conditions. This prompted us to investigate an $AlCl_3$-catalyzed reaction of **1** with **2**. In the present paper we wish to report the results.

The reaction was carried out by adding one mole equiv of $AlCl_3$ to an equimolar mixture of **1** and **2** in CH_2Cl_2 under ice-cooling. This reaction was instantaneous in most cases (as shown by a color change and the evolution of HCl gas) and came to completion upon briefly heating at ca. 40 °C. Through the reaction with **2**, the corresponding 2-arylthiophenes (**3**) and 5-chloro-2,2′-bithienyl (**5**) were obtained as the main products. On occasions, the 2,4-diarylthiophenes (**4**) and its tetrahydrothiophene derivatives (**7**) were isolated from the products. In many cases, the presence of isomers due to the

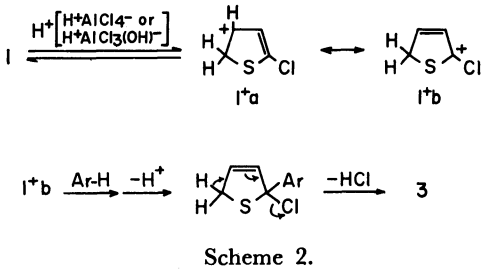
Table 1. Reaction of 2-Chlorothiophene (**1**) with Aromatic Compounds (**2**)[a)]

Ar–H (**2**)	Mole ratio **1**/**2**/$AlCl_3$	Yield/ %[b)] **3**	**4**	**5**	Bp ((θ_b/°C)/mmHg) or Mp (θ_m/°C)(lit,)
a: C_6H_6	1:5:1	Tr[c)]		42	**5:** Bp 110—120/4 (100—110/3—4[4)])
b: $C_6H_5CH_3$	1:5:1	3		25	**3b:** R=4-CH_3, R′=H; Mp 61—63 (63—64[15b)], 63—66[17)], 82—83[18b)])
c: *m*-$C_6H_4(CH_3)_2$	1:3:1	20		34	**3c:** R=R′=2,4-$(CH_3)_2$; Bp 61—63/1×10^{-4}
d: $C_6H_5OCH_3$	1:1:1	44	2	22	**3d:** R=4-OCH_3, R′=H; Mp 109—110 (110—111[4)], 107—108[16)])
	1:5:1	30	15	Tr	**4d:** R=4-OCH_3, R′=H; Mp 219—221 (204—205[9a)], 217—219[9b)])
	1:5:0.5	20	9		
e: *o*-$CH_3C_6H_4OCH_3$	1:1:1	51[f)]	2[d)]	6	**3e:** R=CH_3, R′=OCH_3; Mp 58—67
f: *m*-$CH_3C_6H_4OCH_3$	1:1:1	53[f)]	3[d)]	10	**3f:** R=CH_3, R′=OCH_3; Oil
g: *m*-$C_6H_4(OCH_3)_2$	1:1:1	55	2[d)]	Tr	**3g:** R=R′=2,4-$(OCH_3)_2$; Bp 124—126/5×10^{-4}
	1:3:1	38	28[d)]	Tr	**7g:** R=R′=2,4-$(OCH_3)_2$; Mp 113—114
h: $C_{10}H_8$[e)]	1:1:1	13[f)]		35	**3h:** Ar=naphthyl; Oil[h)]
i: α-$C_{10}H_7OCH_3$[g)]	1:1:1	83		Tr	**3i:** R=4-OCH_3; Mp 50—51
j: β-$C_{10}H_7OC_2H_5$[g)]	1:1:1	59		8	**3j:** R=2-OC_2H_5; Mp 58—59

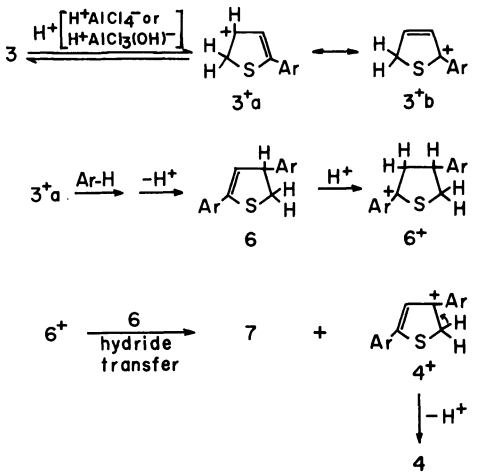
a) Reaction conditions: 30 min under ice-cooling, then 60 min at room temperature, and additional 30 min at ca. 40 °C. b) Isolated yield based on **1** used. c) Trace. d) Contains the corresponding dihydro (**6**) and tetrahydro derivatives (**7**). e) Naphthalene. f) A mixture of the positional isomers. g) $C_{10}H_7$-: naphthyl. h) 2-(2-Naphthyl)thiophene (main component) was isolated from the mixture, mp 104—105 °C (lit,[15b)] 104—105 °C).



Scheme 1.



Scheme 2.



Scheme 3.

position of the substituent(s) on the aromatic ring, the dihydrothiophene derivatives (**6**) of **4**, and the coupling products of **3**, probably 5,5′-diaryl-2,3′-bithienyls (**8**),[6] were also suggested in the products (MS, NMR, and/or TLC). The results are summarized in Table 1.

The yields of the products and the product distribution depend on the relative reactivities of **2** and **1** towards electrophiles and the mole ratio of **2** to **1**. Thus, with substrates less reactive than **1**, predominantly the self-condensation of **1** occurred. For example, in a reaction with benzene (**2a**), **5** was obtained as the sole isolable product in ca. 40% yield, which had been prepared from 2-iodothiophene in seven steps.[7] With reactive substrates such as aryl alkyl ethers, the coupling of **1** with aromatic rings predominated, yielding **3** as expected. This sometimes further reacted with **2** (or **3**) to give **4**, **6**, and **7** (or **8**). An increasing mole ratio of **2** produced higher yields of **4** and its analogs.

The structures of the products were confirmed by their physical and spectral data, elemental analyses and/or direct comparisons with the authentic samples. Authentic samples of 2-(4-methoxy-1-naphthyl)- (**3i**) and 2-(2-ethoxy-1-naphthyl)thiophenes (**3j**) were conveniently prepared by Grignard cross-coupling between 2-thienylmagnesium iodide and the corresponding 1-iodo-4- or 1-iodo-2-alkoxynaphthalene using nickel(II) acetylacetonate as a catalyst.[8] Usually, compounds, **4**, **6**, and **7**, were obtained as mixtures from the products. The presence of the three compounds was readily shown by the MS spectra of the mixtures. It was difficult to separate the mixtures into their components, but 2,4-bis(*p*-methoxyphenyl)thiophene (**4d**) and 2,4-bis(2,4-dimethoxyphenyl)tetrahydrothiophene (**7g**) could be isolated from mixtures which were produced in reactions of **1** with excess anisole (**2d**) and with excess resorcinol dimethyl ether (**2g**), respectively. The structure of **4d** was established by a comparison of its melting point and UV spectral data with that reported in the literature.[9] The structure of **7g** was assigned on the basis of spectral data and elemental analyses. The MS [*m/z* 360 (M^+, 100%)] and UV spectra [λ_{max} (MeOH) 231 (4.29), 277 (3.78)] suggested the presence of two dimethoxyphenyl units in the molecule of **7g**, neither of which was in conjugation. The ^{1}H NMR spectrum ($CDCl_3$) exhibited, besides a resonance involving six protons of the two aromatic groups, the characteristic peaks for a 2,4-disubstituted tetrahydrothiophene ring in the aliphatic region;[10] a two-proton multiplet (δ 1.93—2.63) and signals (δ 3.03 and 3.21) ascribable to the AB part of an ABX spin system corresponding to 3- and 5-methylene protons. A one-proton multiplet (centered at δ ca. 3.7) and a quartet (δ 5.02, the X part of the ABX system) were ascribable to the 4- and 2-methine groups, respectively. Although 2,4-disubstituted tetrahydrothiophenes exist in two diastereomeric forms, cis and trans, and in each case there are many conformational isomers as a result of the so-called pseudorotation, a detailed examination of the structure of **7g** was not further undertaken. An attempted dehydrogenation of **7g** to **4g** with chloranil was unsuccessful. The dihydrothiophene derivatives (**6**) could not be isolated, but the ^{1}H NMR spectra of the

mixtures showed the olefinic proton absorption (δ ca. 6.0) expected for **6**.[11]

A probable mechanism for the formation of **3** is shown in Scheme 2; this requires an initial protonation of **1** to form 2-chlorothiophenium ion **1⁺b** as the electrophile. It is widely accepted that $AlCl_3$, when contacted with water in moist air, forms species such as $H^+AlCl_3(OH)^-$, which act as proton sources. In this reaction, once a small amount of **3** had been formed, the reaction could provide HCl, which, together with $AlCl_3$, would prompt a further reaction. Thiophenium ions produced from several thiophene derivatives have been observed directly by means of ^1H NMR spectroscopy.[12] We have also confirmed the presence of the ion **1⁺** in an $AlCl_3$–HCl–CH_2Cl_2 system at −40 °C by a direct NMR spectroscopic observation.[13] With less reactive substrates than **1**, the carbonium ion **1⁺b** attacks, instead of the substrate, another molecule of **1**, generating **5** as the main product. 100% Orthophosphoric acid (PPA) failed to cause a reaction with anisole at room temperature; this is probably due to the lower catalytic activity or a smaller acid strength of PPA than that of $H^+AlCl_3(OH)^-$ and/or $H^+AlCl_4^-$.

The protonation of **3** produces carbonium ions, **3⁺a** and **3⁺b**. An attack of **3⁺a** upon an aromatic substrate, followed by proton elimination, gives the corresponding dihydrothiophene **6**. A hydride transfer from **6** to **6⁺** affords the tetrahydrothiophene **7** and the carbonium ion **4⁺**, which then yields the 2,4-diarylthiophene **4** by the elimination of a proton (Scheme 3). Compound **8** can be formed analogously to **4**.

In conclusion, it was found that in the presence of $AlCl_3$ **1** was sufficiently activated to react with various active aromatic compounds under mild conditions, giving the corresponding 2-arylthiophenes (**3**) as the major products. The results are of interest not only from a theoretical viewpoint concerning the unusual reactivity of the chlorine atom of **1**, but also from a preparative one. Thus, a series of 2-arylthiophenes with alkoxyl group(s) on the aromatic ring not readily accessible by the known procedures[14] was prepared in one step by this reaction using **1** as a starting substance in moderate to good yields.

Experimental

All melting and boiling points are uncorrected. The NMR, UV, IR, and MS spectra were obtained on Hitachi R-22 (90 MHz, TMS as an internal reference), Hitachi EPU-2A, Hitachi EPI-S2, and Hitachi UMU (70 eV) spectrometers, respectively.

2-Chlorothiophene (**1**) was prepared by a method described in the literature.[19] Commercial $AlCl_3$ was used without special precautions against moisture. The authentic 5-chloro-2,2′-bithienyl (**5**),[4] 2-phenylthiophene (**3a**),[20] and 2-(*p*-methoxyphenyl)thiophene (**3d**)[4] were prepared according to the literature.

Reaction of 2-Chlorothiophene (1) with Resorcinol Dimetyl Ether (2g) (Typical Procedure). Pulverized $AlCl_3$ (2.7 g, 20 mmol) was added in portions to ice-cooled solutions of **1** (2.4 g, 20 mmol) and **2g** (2.8 g, 20 mmol) in CH_2Cl_2 (10 ml) over 2—3 min periods. Exothermic reactions occurred with the appearance of a coloration of the reaction mixtures. Also, the temperature of the mixtures rose to ca. 20 °C. The reaction mixtures were stirred in the ice-bath for 30 min, then at room temperature for 60 min, and finally at the reflux temperature of the solvent for additional 30 min. An evolution of HCl gas was observed during the reactions. Reaction mixtures were poured into ice-water (ca. 70 ml) and extracted with $CHCl_3$ (20 ml×3). The extracts were combined, washed successively with water, 5% $NaHCO_3$ solution, and water, and dried (Na_2SO_4). After the removal of the solvent and small amounts of the starting substances by distillation, the residues were chromatographed (silica gel/benzene–hexane (3:2)) to afford 2-(2,4-dimethoxyphenyl)thiophene (**3g**; 2.4 g) and an oily mixture (0.14 g) of 2,4-bis(2,4-dimethoxyphenyl)thiophene (**4g**), 2,4-bis(2,4-dimethoxyphenyl)dihydrothiophene (**6g**), and 2,4-bis(2,4-dimethoxyphenyl)tetrahydrothiophene (**7g**).

When **1** was reacted with three equivalent moles of **2g** in the presence of an equimolar amount of $AlCl_3$, the yield of the oily mixture increased; for the mixture, bp 215—220 °C/1×10^{-3} mmHg (1 mmHg≈133.322 Pa). MS *m/z* (rel. intensity) 356 (M^+ for **4g**, 100), 358 (M^+ for **6g**, 22), 360 (M^+ for **7g**, 37). Found: C, 66.82; H, 6.13%. The oily mixture was diluted with a mixture of MeOH and acetone and left standing in the cold to give **7g**.

3g: Colorless viscous oil, bp 124—126 °C/5×10^{-4} mmHg. MS *m/z* 220 (M^+, 100). UV λ_{max} (MeOH) 226 sh (4.07), 279—287 (4.09), 310 (4.05). ^1H NMR (CCl_4) δ=3.71, 3.80 (s, 3H each, OCH_3), 6.25—6.5 (m, 2H, Ar-H), 6.8—7.5 (m, 4H, Ar-H). Found: C, 65.53; H, 5.50%. Calcd for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49%.

7g: Colorless fine needles, mp 113—114 °C (from MeOH). MS *m/z* 360 (M^+, 100). UV λ_{max} (MeOH) 231 (4.29), 277 (3.78). ^1H NMR ($CDCl_3$) δ=1.93—2.63 (m, 2H, 3-H_aH_b), 3.03, 3.21 (ABX m J_{ab}=9.1 Hz, J_{a4}=5.7 Hz, J_{b4}=10.7 Hz, 2H, 5-H_aH_b), 3.58~ (m, overlapped partly with the OCH_3 peaks, 4-H), 3.76, 3.79 (s, 6H each, OCH_3) 5.02 (ABX q, $J_{a4}+J_{b4}$=16.4 Hz, 1H, 2-H), 6.38—6.56 (m, 4 H, Ar-H) 7.13—7.23, 7.50—7.59 (m, 1H each, Ar-H). Found: C, 66.55; H, 6.78%. Calcd for $C_{20}H_{24}O_4S$: C, 66.63; H, 6.71%.

Reaction with Anisole (2d). The reaction mixture which was obtained by the reaction of **1** (30 mmol) with 5 mol equiv of **2d** and 1 mol equiv of $AlCl_3$ was poured into ice-water. 2,4-Bis(*p*-methoxyphenyl)thiophene (**4d**; 1.4 g, mp 211—220 °C), thus precipitated, were filtered off and washed with $CHCl_3$ (10 ml). The organic layer was separated from the filtrate and combined with the washing. After the usual work-up and the removal of solvents and starting substances by distillation, the residue was chromatographed (silica gel/benzene–hexane (3:1)) to give 2-(*p*-methoxyphenyl)thiophene (**3d**; after recrystallization from MeOH, 1.7 g, mp 109—110 °C) and 2,4-bis(*p*-methoxyphenyl)tetrahydrothiophene (**7d**; 0.4 g, oil, MS *m/z* 300

(M^+, 20), ^1H NMR (CCl_4) δ=2.0—2.7 (m, 2H), 3.0—3.4 (m, 2H), 3.5~ (m, overlapped in part with the OCH_3 peaks), 3.82 (s, 6H), 4.4—4.9 (m, 1H), 6.7—7.6 (m, 8H)). The presence of the corresponding diarylbithienyl (**8d**) and 2,4-bis(*p*-methoxyphenyl)dihydrothiophene (**6d**) was also suggested to be in the product by an MS spectral analysis.

4d: Colorless leaflet, mp 219—221 °C (from *N,N*-dimethylformamide). MS *m/z* 296 (M^+, 100). UV λ_{max} (EtOH) 267 (4.60), 292 sh (4.28), 310 sh (3.98) (lit,[9a] 265 (4.56), 300—330 (4.18—4.04)).

Reaction with *o*-Methoxytoluene (2e). Chromatography (silica gel/benzene–hexane (1:2)) of the crude product gave an unseparable mixture of the two isomeric 2-(methoxytolyl)thiophenes (**3e**; mp 58—67 °C, the ratio= 85:15 (NMR)) together with small amounts of **5** and a mixture of the corresponding diarylthiophenes (**4e**; MS *m/z* 324 (M^+, 100)).

3e (as a mixture): Pale yellow crystals, mp 67—70 °C (from hexane). MS *m/z* 204 (M^+, 100). ^1H NMR (CCl_4) δ=2.11, 2.15 (s each, 3H, CH_3), 3.76 (s, 3H, OCH_3), 6.6—7.4 (m, 6H, Ar–H). Found: C, 70.31; H, 5.94%. Calcd for $C_{12}H_{12}OS$: C, 70.55; H, 5.92%.

Reaction with *m*-Methoxytoluene (2f). The crude products were chromatographed (silica gel/benzene–hexane (1:1)) to give an unseparable mixture of the two isomeric 2-(methoxytolyl)thiophenes (**3f**; oil, the ratio=70:30 (NMR)) together with small amounts of **5** and a mixture of the corresponding diarylthiophene (**4f**) and diaryldihydrothiophene (**6f**) (MS *m/z* 324 (M^+ for **4f**, 31), 326 (M^+ for **6f**, 26)).

3f (as a mixture): Pale yellow viscous oil, bp 100—110 °C/2×10^{-3} mmHg. MS *m/z* 204 (M^+, 86). ^1H NMR (CCl_4) δ=2.31 (s, 3H, CH_3), 3.74, 3.86 (s each, 3H, OCH_3), 6.5—7.5 (m, 6H, Ar–H). Found: C, 70.68; H, 5.91%. Calcd for $C_{12}H_{12}OS$: C, 70.55; H, 5.92%.

Reaction with 1-Methoxy- (2i) or 2-Ethoxynaphthalene (2j). The crude products were chromatographed (silica gel/hexane–$CHCl_3$ (3:1)) to afford 2-(4-methoxy-1-naphthyl)- (**3i**) or 2-(2-ethoxy-1-naphthyl)thiophene (**3j**), respectively. The IR spectra were identical with those of the authentic samples which were prepared as described below, and the mixed melting points exhibited no depression.

3i: Colorless plates, mp 50—51 °C (from MeOH). MS *m/z* 240 (M^+, 100). UV λ_{max} (MeOH) 218 (4.57), 238 sh (4.37), 310 (4.02). ^1H NMR ($CDCl_3$) δ=4.00 (s, 3H, OCH_3), 6.83 (d, 1H, Ar–H), 7.1—7.3 (m, 2H, Ar–H), 7.3—7.6 (m, 4H, Ar–H), 8.1—8.5 (m, 2H, Ar–H). Found: C, 75.15; H, 5.01%. Calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.03%.

3j: Pale yellow needles, mp 58—59 °C (from MeOH). MS *m/z* 254 (M^+, 100). UV λ_{max} (MeOH) 232 (4.71), 283 (3.80), 294 (3.81), 337 (3.60). ^1H NMR (CCl_4) δ=1.24 (t, *J*=6.6 Hz, 3H, $OCH_2\underline{CH_3}$), 4.04 (q, *J*=6.6 Hz, 2H, $O\underline{CH_2}CH_3$), 6.9—7.4 (m, 6H, Ar–H), 7.6—7.8 (m, 3H, Ar–H). Found: C, 75.85; H, 5.62%. Calcd for $C_{16}H_{14}OS$: 75.56; H, 5.55%.

Preparation of 2-(4-Methoxy-1-naphthyl)- (3i) and 2-(2-Ethoxy-1-naphthyl)thiophenes (3j) by the Grignard Cross-Coupling. The procedure was a modification of the method used for the preparation of arylnaphthalenes from iodonaphthalenes.[8] A solution of 2-iodothiophene (7.6 g, 36 mmol) in dry ether (40 ml) was added under a nitrogen atmosphere to magnesium turnings (0.87 g, 36 mmol) in a flask at such a rate that a gentle reflux was maintained (ca. 20 min). After an additional 1-h heating, the resulting Grignard solution was diluted with dry benzene (20 ml). To the refluxing solution was added a solution of 1-iodo-4-methoxynaphthalene[21] (3.4 g, 12 mmol) and nickel(II) acetylacetonate (31 mg) in dry benzene (20 ml). The reaction mixture was stirred for 1 h at the reflux temperature. After cooling, the mixture was treated with an aqueous NH_4Cl solution (20%, 100 ml), and the aqueous layer was extracted with benzene (20 ml×2). The combined organic layers were washed with water and dried. After a removal of the solvents, the crude reaction products were chromatographed (silica gel/hexane–$CHCl_3$ (3:1)) to give 2,2′-bithienyl (mp 32.5—33.5 °C; 0.8 g) and crude **3i** (mp 46—49 °C; 2.4 g, 88%) in order of decreasing R_f values. This was recrystallized from MeOH to afford the analytical sample (mp 50—51 °C).

2-(2-Ethoxy-1-naphthyl)thiophene (**3j**) was prepared similarly by the reaction of 2-thienylmagnesium iodide and 1-iodo-2-ethoxynaphthalene[22] in 75% yield. Mp 58—59 °C (from MeOH).

Preparation of 2-(2,4-Dimethylphenyl)thiophene (3c) by Gomberg Reaction. Compound **3c** was prepared by a reaction of thiophene with 2,4-dimethylbenzenediazonium acetate according to the procedure of Beaton et al.[18b] Purification of the crude product by chromatography (silica gel/CCl_4) followed by distillation afforded **3c** (13%) as a colorless oil. Bp 61—63 °C/1×10^{-4} mmHg. MS *m/z* 188 (M^+, 100). UV λ_{max} (EtOH) 229 (4.03), 268 (4.03); ^1H NMR (CCl_4) δ=2.29 (s, 3H, CH_3), 2.31 (s, 3H CH_3), 6.90—7.23 (m, 6H, Ar–H). Found: C, 76.40; H, 6.39%. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42%.

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6) Acid-catalyzed reaction of certain 2-arylthiophenes (**3**) has been known to afford the corresponding 5,5′-diaryl-2,3′-bithienyls (**8**); see Part IV of this series.[1]

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14) 2-Arylthiophenes with substituent(s) on the aromatic ring have been prepared by: a) The cyclization of the sodium salts of appropriately substituted benzoylpropionic acids with P_2S_3 or P_4S_7,[15] b) The coupling of 2-thienylcopper[16] or 2-thiophenecarboxylic acid[17] with iodoarenes, and c) The Gomberg reaction between arenediazonium salts and thiophene.[18] However, these methods require many steps and the yields are low.

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