Reactions of 2-Chlorothiophene with Cation Exchange Resin and 100% Orthophosphoric Acid. Formation of the Dimer Type Products Containing a Tetrahydro-2-thiophenone Moiety[1)]

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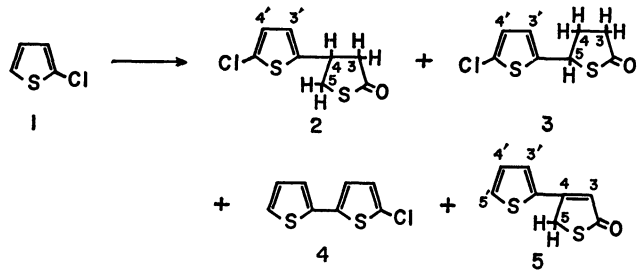
It has been found that 2-chlorothiophene is converted into the dimer type products by Amberlyst 15 or 100% orthophosphoric acid, the reaction yielding 4- and 5-(5-chloro-2-thienyl)tetrahydro-2-thiophenones and 4-(2-thienyl)-2(5*H*)-thiophenone together with 5-chloro-2,2′-bithienyl. The distribution of the products is considerably affected by the acid used and in the presence of phenol or anisole the reaction affords additionally 4-[5-(*p*-hydroxyphenyl)-2-thienyl]tetrahydro-2-thiophenone or 4-[5-(*p*-methoxyphenyl)-2-thienyl]tetrahydro-2-thiophenone, respectively.

Simple thiophenes have been known to polymerize on treatment with certain acidic materials;[2)] in most cases amorphous, highly insoluble polymers were obtained. Since the products may form a potential source of oligothienylenes, efforts have been made to produce simple oligomers by the use of this type of reaction. Moreover, the oligomerization may supply information regarding the reactivity of thiophene as a conjugated diene which has not been well understood. However, few reports have appeared in the literature, *e.g.*, thiophene reacts with 100% orthophosphoric acid to yield the so-called "thiophene trimers" and "pentamer,"[3)] and with sulfuryl chloride and iron powder to yield the chlorinated bithienyls.[4)]

A novel reaction will be reported here, namely, the reaction of 2-chlorothiophene (**1**) with cation exchange resin and 100% orthophosphoric acid leading to dimer type products containing a tetrahydro-2-thiophenone ring. This result is in contrast to that obtained by the reactions of **1** with sulfuric acid,[5)] and aluminium chloride and copper(II) chloride;[6)] in both cases the major product obtained even under mild conditions was a polymeric material possessing a complicated structure. This reaction also offers a novel example of the conversion of thiophenes to other heterocycles.

2-Chlorothiophene (**1**) was treated with half its own weight of Amberlyst 15 at 120 °C for 4 h. Evolution of hydrogen chloride gas was observed during the reaction. The oily product was shown by thin-layer chromatography (TLC) to consist of two principal components, which were isolated by column chromatography. The component of high R_f value was found to be 5-chloro-2,2′-bithienyl (**4**, 21% based on reacted **1** at 70% conversion) by comparison with the authentic sample. Careful chromatography of the component of low R_f value gave 4-(5-chloro-2-thienyl)tetrahydro-2-thiophenone(**2**, 34%) as a colorless oil together with a small amount of 5-(5-chloro-2-thienyl)tetrahydro-2-thiophenone (**3**, 3.5 %) as colorless crystals. Some 4-(2-thienyl)-2(5*H*)-thiophenone (**5**, 1.5%) was also isolated.

Similar treatment of **1** with an equivalent weight of freshly prepared 100% orthophosphoric acid afforded the same products at 82% conversion. The distribution of products, however, was different from that with Amberlyst 15, *i.e.*, **2** (11.5%), **3** (11%), **4** (7%), and **5** (≈1%), respectively (Scheme 1).



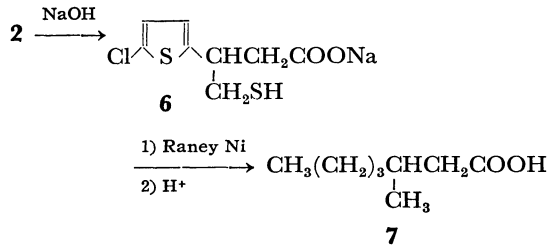
Scheme 1.

The structures of the thiophenones have been assigned on the basis of the following evidence.

The IR spectrum (CCl_4) of **2** indicated carbonyl absorption at 1715 cm^{-1} but no absorption attributable to hydroxyl groups. The UV spectrum [λ_{max}(MeOH) 242 nm (log ε 4.07)] suggested an unconjugated thiophene ring. Compound **2** did not react with ordinary ketonic reagents. When heated with dilute sodium hydroxide solution, it easily dissolved producing a clear solution, but was partially regenerated from the alkaline solution on acidification with hydrochloric acid. The mass spectrum showed the molecular ion at *m/e* 218 (relative intensity 72%) and characteristic M+2 peak (30%) indicative of a structure containing two sulfur atoms and one chlorine atom. Other prominent peaks were *m/e* 144 (base peak; M^+-CH_2SCO) and 109 ($M^+-CH_2SCO-Cl$). These findings suggest a tetrahydro-2-thiophenone substituted by a 5-chloro-2-thienyl moiety. The NMR spectrum (CCl_4) showed, in addition to an AB quartet (J=3.8 Hz) for the two protons of 2,5-disubstituted thiophene ring,[7)] a typical AB octet (centered at approx. δ 2.7) of an ABX spin system for a methylene group, and a three-proton multiplet (δ 3.2—4.1) due to the methine (the X-proton of the ABX system) and a methylene group. The large geminal coupling constant ($J_{a,b}$=16.6 Hz) of the AB octet together with the position indicated that the methylene proton were adjacent to a carbonyl group.[8)] The downfield methylene protons were strongly deshielded indicating that the protons were adjacent to a sulfur atom. Thus the thienyl moiety must be located at the 4-position of the tetrahydro-2-thiophenone ring. A shift reagent [Eu(fod)$_3$] experiment agreed with the assignment; upon addition of the reagent the octet underwent a greater downfield shift and the three-proton multiplet

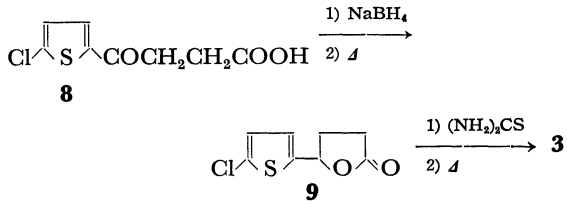
separated with a smaller shift into a one-proton multiplet for the methine proton and an AB octet for the methylene protons.

The structure assignment was substantiated by the alkaline hydrolysis of **2** followed by reductive desulfurization (Raney nickel) of the resulting mercaptoacid (**6**) which gave 3-methylheptanoic acid (**7**), which was identical with an authentic sample (Scheme 2).



Scheme 2.

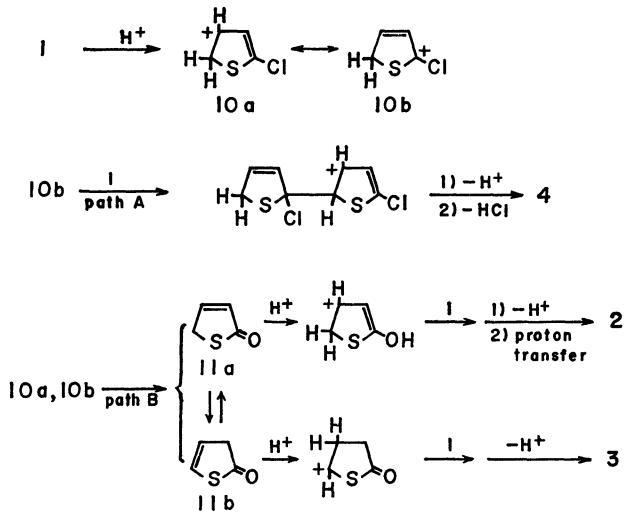
Compound **3** had the same molecular weight as that of **2**, and similar IR (CCl_4; ν_{CO} 1715 cm^{-1}), UV [λ_{max} (MeOH) 244 nm (4.09)], and chemical properties, indicating that **3** is an isomer of **2**. The NMR and mass spectra were appreciably different from that of **2**. The mass spectrum showed significant peaks at *m/e* 218 (base peak; M^+), 158 (M^+ — SCO), 157 (M^+ — SCO — H), and 123 (M^+ — SCO—Cl). The NMR spectrum ($CDCl_3$) exhibited, besides the resonance for two protons of a 2,5-disubstituted thiophene ring, a four-proton multiplet (δ 1.9—3.0) due to two adjacent, similarly shielded methylene groups and a multiplet (δ 5.0—5.3) due to a methine proton. The strongly deshielded position of the methine absorption indicates that the methine proton is adjacent to both the sulfur atom and the thienyl group. Upon gradual addition of the shift reagent the four-proton multiplet separated into two methylene multiplets; one (due to the methylene proton α to the carbonyl group) underwent a greater downfield shift relative to the other (due to the β methylene protons) and the methine multiplet. These facts are compatible with structure **3**, which was finally established by comparison of the spectral data and the melting point with those of an authentic sample synthesized according to Scheme



Scheme 3.

The minor product **5** was thought to contain a thiophene ring conjugated with an enone group on the basis of the UV [λ_{max}(MeOH) 277 (3.96), 327 (4.19)] and IR spectra [KBr; $\nu_{C=C}$ 1600, ν_{CO} 1660 cm^{-1}]. The NMR spectrum ($CDCl_3$) displayed significant resonances as follows; signals for three ring protons, a triplet for an olefinic proton at δ 6.49, and a methylene doublet at δ 4.39. Decoupling of the doublet caused the triplet to collapse to a singlet, indicating that the olefinic and the methylene protons were mutually spin-coupled with a coupling constant J=1.5 Hz in an allylic group (–CH=C–CH_2–). These data together with the mass spectrum [*m/e* 182 (base peak; M^+), 154 (M^+— CO), 153 (M^+— CO — H), 108 (M^+— CH_2SCO)] and the elemental analysis confirmed structure **5**.

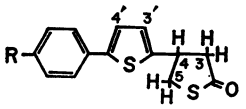
The formation of **4** can be explained by the mechanism illustrated in Scheme 4 (path A). The entire reaction pathway leading to the thiophenone derivatives is not clear at this stage. Of interest in this regard, however, is the fact that both **2** and **3** were formed in the reaction and the **2**/**3** ratio varied considerably depending upon the acid and the reaction conditions employed. A probable mechanism which is compatible with these facts may involve the intermediacy of 2-thiophenone tautomers,[9] 2(5*H*)-(**11a**) and 2(3*H*)-thiophenones (**11b**), in the reaction: protonation of **11a** and **11b** followed by the reaction of the resulting carbonium ions with **1** and then the loss of a proton affords **2** and **3**, respectively (path B). The reaction of **10b** with **11b** would similarly yield **5**. The tautomers could be produced from **1** by a reaction analogous to hydrolytic conversion of chlorocyclopentadiene to the corresponding cyclopentenone.[10]



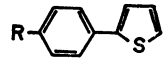
Scheme 4.

It was anticipated from the suggested mechanism that, when the reaction was conducted in the presence of an aromatic compound which is reactive but inert to the resin, the corresponding arylthiophene and/or aryl-substituted tetrahydro-2-thiophenone would be formed. Thus, in the presence of an equimolar amount of phenol the reaction using Amberlyst 15 as an acid resulted in 73% conversion of **1** yielding 4-[5-(*p*-hydroxyphenyl)-2-thienyl]tetrahydro-2-thiophenone (**12**; 28% based on reacted **1**) in addition to **2** (22%) and **4** (7%). The presence of 2-(hydroxyphenyl)thiophene (presumably **13**) and 4-[(*p*-)hydroxyphenyl]tetrahydro-2-thiophenone as the minor products were also detected by mass spectral analysis. Similarly, the reaction in the presence of anisole afforded 4-[5-(*p*-methoxyphenyl)-2-thienyl]tetrahydro-2-thiophenone (**14**; 17% based on reacted **1** at 46% conversion), 2-(*p*-methoxyphenyl)thiophene (**15**;

10%), **2** (20%), and **4** (6%). The structure of **12** and **14** have been assigned on the basis of their mass and NMR spectra, which indicated the presence of one *p*-substituted phenyl, one 2,5-disubstituted thiophene, and one 4-substituted tetrahydro-2-thiophenone ring. The formation of the unexpected tetrahydro-2-thiophenones, **12** and **14**, can be accounted for by a process similar to that of the formation of **2** as shown in Scheme 4. This involves the initial formation of arylthiophene intermediates, **13** and **15**, which react with the protonated **11a** to afford **12** and **14**, respectively.



12: R=OH
14: R=OCH_3



13: R=OH
15: R=OCH_3

In conclusion, it was found that the dimer type products consisting of the unexpected thiophenone derivatives (**2**, **3**, and **5**) and the coupling product (**4**) were formed in the acid-catalyzed reaction of **1** with a cation exchange resin and 100% orthophosphoric acid. In the reaction the thiophene ring clearly behaves as a conjugated diene as well as a heteroaromatic ring. Furthermore, it should be noted that the reaction could be effected with a cation exchange resin. To the authors' knowledge no report in the literature has appeared on the use of cation exchange resins as catalysts for acid-catalyzed oligomerization of aromatic or heteroaromatic nuclei, although the resins have received wide application in organic reactions. It is possible that simple oligomers are formed in the reactions of other properly substituted thiophenes with the resins as well.

Experimental

All melting and boiling points are uncorrected. The NMR spectra were obtained on a Hitachi R-22 spectrometer at 90 MHz, using TMS as an internal reference. The UV, IR, and mass (70 eV) spectra were recorded on Hitachi EPU-2A, Hitachi EPI-S2, and Hitachi UMU-6MG spectrometers, respectively.

2-Chlorothiophene (**1**) was prepared by the method described in the literature.[11] Commercial Amberlyst 15 was used without any treatment. In drying the Amberlyst over phosphorus pentaoxide (115 °C/10—15 mmHg, 24 h), 2—3% weight loss was observed, which was presumably due to loss of water.

*Reaction of **1** with Cation Exchange Resin.* A suspension of Amberlyst 15 (5 g) in **1** (10 g, 0.0843 mol) was stirred at 120 °C for 4 h. Evolution of hydrogen chloride was observed during the reaction. The reaction mixture was extracted with chloroform in a Soxhlet extractor. After the solvent and the unchanged **1** (3.0 g) were distilled off, the residual oil was chromatographed (silica gel, benzene) to give three fractions which are in order of decreasing R_f values: 1) the chlorinated 2,2′-bithienyl, **4**, (1.3 g, 21% based on **1** reacted; contaminated with a small amount of another isomer as shown by GLC), bp 100—110 °C (bath)/3—4 mmHg (lit,[12] 55 °C (bath)/0.05 mmHg); 2) a mixture of the tetrahydrothiophenones, **2** and **3**, (2.4 g, 36%; **2**: **3**=91: 9 as determined by NMR analysis); 3) the thiophenone, **5**, (0.08 g, 1.5%), mp 157—159 °C. The spectral and physical properties are described below.

*Reaction of **1** with 100% Orthophosphoric Acid.* A mixture of **1** (10 g) and the phosphoric acid (prepared immediately prior to use by heating a mixture of 85% orthophosphoric acid (7.5 g) and phosphorus pentaoxide (3 g) at 100 °C for 1 h) was stirred at 110 °C for 6 h. Hydrogen chloride gas was evolved throughout the reaction. After cooling, the greenish brown reaction mixture was poured into cold water, and extracted with chloroform. The extract was washed successively with water, 5% sodium hydrogencarbonate solution and again with water, and dried. After the solvent and unchanged **1** (1.8 g) had been removed, the residual oil was chromatographed (silica gel, benzene) to give **4** (0.5 g, 7%; contaminated with a small amount of another isomer), a mixture of **2** and **3** (1.7 g, 22.5%; **2**: **3**=51: 49), and **5** (0.05 g, ≈1%).

The isomeric tetrahydrothiophenones were separated by repeated chromatography (silica gel, benzene/ligroin (3: 1)).

2: Colorless oil, bp 85—87 °C/5×10^{-4} mmHg. NMR (CCl_4) δ 6.77 (1H, d, $J_{3',4'}$=3.8 Hz, 4′-H), 6.71 (1H, dd, $J_{3',4'}$= 3.8 Hz, $J_{3',4}$=0.7 Hz, 3′-H), 4.1—3.2 (3H, m, 4-H and 5-H_a,H_b), 2.82, 2.62 (2H, ABX octet, $J_{a,b}$=16.6 Hz, $J_{a,4}$=10.1 Hz, $J_{b,4}$=6.6 Hz, 3-H_a,H_b); (CCl_4; in the presence of 0.36 equivalent mol of Eu(fod)$_3$) δ 7.37 (1H, dd, 3′-H), 6.97 (1H, d, 4′-H), 6.76, 6.50 (2H, ABX octet, 3-H_a,H_b), 5.8—5.3 (1H, m, 4-H), 5.06, 4.98 (2H, ABX octet, $J_{a,b}$=11.0 Hz, $J_{a,4}$=8.1 Hz, $J_{b,4}$=6.7 Hz, 5-H_a, H_b). Found: C, 44.05; H, 3.45%. Calcd for $C_8H_7ClOS_2$: C, 43.93; H, 3.23%.

3: Colorless crystals, mp 51.5—52.5 °C (light petroleum ether–ether). NMR ($CDCl_3$) δ 6.83 (1H, dd, $J_{3',4'}$=3.7 Hz, $J_{3',5}$=0.7 Hz, 3′-H), 6.74 (1H, d, $J_{3',4'}$=3.7 Hz, 4′-H) 5.0—5.3 (1H, m, 5-H), 1.9—3.0 (4H, m, 3-H_a,H_b and 4-H_a,H_b); ($CDCl_3$; in the presence of 0.25 equivalent mol of Eu(fod)$_3$ δ 7.20 (1H, dd, 3′-H), 6.91 (1H, d, 4′-H), 5.91 (1H, ABX q, $J_{a,4}+J_{b,4}$=14.4 Hz, 5-H), 5.0—4.3 (2H, m, 3-H_a,H_b), 3.6—2.8 (2H, m, 4-H_a, H_b). Found: C, 43.94; H, 3.03%. Calcd for $C_8H_7ClOS_2$: C, 43.93; H, 3.23%.

5: Pale yellow crystals, mp 165—166 °C (ligroin–benzene). NMR ($CDCl_3$) δ 7.50, 7.39 (2H, ABX octet, $J_{3',5'}$=1.1 Hz, $J_{3',4'}$=3.7 Hz, $J_{4',5'}$=4.8 Hz, 3′-H and 5′-H), 7.11 (1H, ABX q, $J_{3',4'}$=3.7 Hz, $J_{4',5'}$=4.8 Hz, 4′-H), 6.49 (1H, t, $J_{3,5}$=1.5 Hz, 3-H), 4.39 (2H, d, $J_{3,5}$=1.5 Hz, 5-H_2). Found: C, 52.72; H, 3.15%. Calcd for $C_8H_6OS_2$: C, 52.71; H, 3.31%.

*Desulfurization of **2** with Raney Nickel.* The tetrahydrothiophenone **2** (0.93 g, 4.25 mmol) was dissolved in 20% sodium hydroxide solution (50 ml) by heating, and the solution diluted with water (50 ml). W-7 Raney nickel (prepared from 15 g of the alloy) was added to the cooled solution and the mixture stirred at 70 °C for 5 h. The reaction mixture was filtered and the nickel washed with water (300 ml). The filtrate and the washings were combined and evaporated to *ca.* 100 ml. The solution was acidified with hydrochloric acid in the cold to give an oil. Work-up and distillation *in vacuo* afforded 3-methylheptanoic acid (**7**; 0.50 g, 82%) as a colorless liquid, bp 130—140 °C (bath)/15 mmHg (lit,[13] 121 °C/15 mmHg); the IR and NMR spectra were identical with those of the authentic sample.[13]

*5-(5-Chloro-2-thienyl)tetrahydro-2-furanone (**9**).* Sodium borohydride (1.9 g, 0.05 mol) was added with stirring to a mixture of 3-(5-chloro-2-thenoyl)propionic acid[14] (**8**; 10.9 g, 0.05 mol) and sodium hydroxide (1.6 g) in water (80 ml), while the temperature of the reaction mixture being maintained below 40 °C during the addition. The mixture was stirred for 4 h at room temperature, added to water, and acidified with hydrochloric acid. After extraction with ether and the usual work-up, the oily product was distilled under reduced

pressure and the distillate (bp 117—127 °C/1 × 10^{-4} mmHg chromatographed (silica gel, chloroform) to give **9** (4.7 g, 46%) and 4-(5-chloro-2-thienyl)-3-butenoic acid (1.8 g, 17%).

9: Colorless oil, bp 112—114 °C/1 × 10^{-4} mmHg. MS *m/e* 202 (M^+). IR (CCl_4) ν_{CO} 1800 cm^{-1}. NMR ($CDCl_3$) δ 6.83 (1H, d, $J_{3,4'}$=3.8 Hz, thiophene 3'-H), 6.76 (1H, d, $J_{3',4'}$=3.8 Hz, thiophene 4'-H), 5.54 (1H, t, 5-H), 2.9—2.0 (4H, m, 3-H_2 and 4-H_2). Found: C, 47.66; H, 3.48%. Calcd for $C_8H_7ClO_2S$: C, 47.41; H, 3.48%.

4-(5-Chloro-2-thienyl)-3-butenoic Acid: Colorless crystals, mp 84—85 °C (benzene–hexane). MS *m/e* 202 (M^+). IR (KBr) ν_{CO} 1700 cm^{-1}. NMR ($CDCl_3$) δ 9.97 (1H, br s, COOH), 6.71 (1H, d, $J_{3',4'}$=4.0 Hz, thiophene 4'-H), 6.64 (1H, d, $J_{3',4'}$=4.0 Hz, thiophene 3'-H), 6.47 (1H, dd, $J_{3,4}$=15.9 Hz, $J_{2,4}$=1.0 Hz, 4-H), 5.92 (1H, dt, $J_{3,4}$=15.9 Hz, $J_{2,3}$=7.0 Hz, 3-H), 3.19 (2H, dd, $J_{2,3}$=7.0 Hz, $J_{2,4}$=1.0 Hz, 2-CH_2). Found: C, 47.34; H, 3.46%. Calcd for $C_8H_7ClO_2S$: C, 47.41; H, 3.48%.

Preparation of 3 from 9. To a suspension of the lactone **9** (1.0 g, 5 mmol) in 48% hydrobromic acid (2.5 g) was added thiourea (0.4 g, 5 mmol) with shaking. A white solid formed within several minutes and was allowed to stand overnight. A sodium hydroxide solution (0.6 g, in 5 ml of water) was added and the mixture gently refluxed for 70 min. The organic layer was separated, and the aqueous layer acidified and extracted with ether. The organic layer and the ether extracts were combined and dried. After removal of the solvent the residual oil was heated at 160—170 °C under reduced pressure (20 mmHg) for 1 h. The oily product was chromatographed (silica gel, chloroform/benzene (4: 1)) to give **3** (mp 51—52 °C; 160 mg, 15%). The IR and NMR spectra were identical with those of **3** obtained by the acid-catalyzed reaction of **1**, and the mixed melting point exhibited no depression.

Reaction of 1 with Cation Exchange Resin in the Presence of Phenol. A mixture of **1** (4.8 g, 0.04 mol), phenol (3.8 g, 0.04 mol) and Amberlyst 15 (2.4 g) was stirred at 120 °C for 4 h. The dark brown reaction mixture was extracted with aceton in a Soxhlet extractor. After removal of the solvent the unchanged **1** (1.3 g) and phenol (1.9 g) were recovered by distillation under reduced pressure. The residual oil was chromatographed (silica gel, benzene/acetone (9: 1)) to give 4-[5-(*p*-hydroxyphenyl)-2-thienyl]tetrahydro-2-thiophenone (**12**; mp 159—166 °C, 1.1 g, 28% based on reacted **1**), **2** (0.7 g, 22%), **4** (0.2 g, 7%), and polymeric material (0.8 g) Mass spectroscopy suggested the presence of 4-[(*p*-)hydroxyphenyl]tetrahydro-2-thiophenone [*m/e* 194 (M^+), 120 ($M^+ - CH_2SCO$)] and 2-[(*p*-)hydroxyphenyl]thiophene [**13**; *m/e* 176 (M^+), 147 (M^+-CO-H), 131 (M^+-HCS), 115 ($M^+-CO-H-S$)], which were isolated in the impure form by preparative TLC. There was, however, insufficient material for further purification.

12: Pale yellow crystals, mp 171—172 °C (methanol). MS *m/e* 276 (M^+), 202 (M^+-CH_2SCO), 45 (base peak; HCS^+). UV λ_{max}^{MeOH} 304 (4.22). IR (KBr) ν_{CO} 1660, ν_{OH} 3225 cm^{-1}. NMR ($(CD_3)_2CO$): δ 8.46 (1H, s, OH), 7.48, 7.39 (2H, AA'XX' m, *p*-substituted phenyl), 7.10 (1H, d, $J_{3',4'}$=3.8 Hz, 4'-H), 6.96 (1H, dd, $J_{3',4'}$=3.8 Hz, $J_{3',4}$=1.0 Hz, 3'-H), 6.90, 6.80 (2H, AA'XX' m, *p*-substituted phenyl), 4.2—3.2 (3H, m, 4-H and 5-H_a, H_b), 2.92, 2.80 (2H, ABX octet, $J_{a,b}$=16.7 Hz, $J_{a,4}$=10.0 Hz, $J_{b,4}$=7.2 Hz, 3-H_a,H_b). Found: C, 61.01; H, 3.97%. Calcd for $C_{14}H_{12}O_2S_2$: C, 60.84; H, 4.37%.

Reaction of 1 with Cation Exchange Resin in the Presence of Anisole. A mixture of **1** (4.8 g, 0.04 mol), anisole (4.3 g, 0.04 mol) and Amberlyst 15 (2.4 g) was stirred at 120 °C for 4 h and the reaction mixture extracted with chloroform in a Soxhlet extractor. After removal of the solvent, the unchanged **1** (2.6 g) and anisole (3.3 g) were recovered by distillation under reduced pressure. The residual oil was chromatographed (silica gel, hexane/acetone (4: 1)) to afford 4-[5-(*p*-methoxyphenyl)-2-thienyl]tetrahydro-2-thiophenone (**14**; mp 104—107 °C; 0.45 g, 17% based on reacted **1**), 2-(*p*-methoxyphenyl)thiophene (**15**; mp 101—103 °C; 0.35 g, 10%), **2** (0.4 g, 20%), and **4** (0.1 g, 6%). Other traces were detected by TLC but colud not be separated.

15: Colorless crystals, mp 110—111 °C (methanol; lit,[15] 107—108 °C). MS *m/e* 190 (base peak, M^+), 175 (M^+-CH_3), 147 (M^+-CH_3-CO). NMR ($CDCl_3$) δ 7.51, 7.42 (2H, AA'-XX' m, *p*-substituted phenyl), 7.2—6.9 (3H, m, monosubstituted thiophene), 6.89, 6.80 (2H, AA'XX' m, *p*-substituted phenyl), 3.79 (3H, s, $-OCH_3$).

14: Pale yellow crystals, mp 115—116 °C (methanol). MS *m/e* 290 (base peak, M^+), 216 (M^+-CH_2SCO), 201 ($M^+-CH_2SCO-CH_3$), 173 ($M^+-CH_2SCO-CH_3-CO$). UV λ_{max}^{MeOH} 300 (4.36). IR (KBr) ν_{CO} 1705 cm^{-1}. NMR ($CDCl_3$) δ, 7.51, 7.41 (2H, AA'XX' m, *p*-substituted phenyl), 7.01 (1H, d $J_{3',4'}$=3.7 Hz, 4'-H), 6.94, 6.84 (2H, AA'XX' m, *p*-substituted phenyl), 6.84 (1H, dd, $J_{3',4'}$=3.7 Hz, $J_{3',4}$=0.9 Hz, 3'-H), 3.80 (1H, s, $-OCH_3$), 4.4—3.3 (1H, m, 4-H and 5-H_a,H_b), 2.92, 2.77 (2H, ABX octet, $J_{a,b}$=16.8 Hz, $J_{a,4}$=11.0 Hz, $J_{b,4}$=6.0 Hz, 3-H_a,H_b). Found: C, 62.28; H, 4.67%. Calcd for $C_{15}H_{14}O_2S_2$: C, 62.03; H, 4.87%.

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