butenyl bromide, 100 mg of potassium iodide, and 516 mg of *N,N*-diisopropylethylamine in 30 mL of dimethylformamide was heated at 90 °C for 5 h. After the reaction mixture had cooled to room temperature, 100 mL of an aqueous ammonium chloride solution was added and the mixture was extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a crude yellow oil. The oil was purified by flash chromatography, using an 8% ethyl acetate–hexane mixture as the eluent. The major fraction contained 398 mg (82%) of a nearly colorless oil. Distillation of this material (bp 80 °C (0.04 mm)) gave a colorless oil, which was assigned as 2-phenyl-4-methyl-4-(3-methyl-2-butenyl)-Δ^2-oxazolin-5-one (**39**) on the basis of the following data: NMR (CCl_4, 90 MHz) δ 1.47 (s, 3 H), 1.63 (s, 6 H), 2.49 (d, 2 H, J = 8 Hz), 5.02 (t, 1 H, J = 8 Hz), 7.3–8.0 (m, 5 H); IR (neat) 3085, 3065, 3000, 2960, 2940, 1805, 1650, 1620, 1580, 1505, 1464, 1400, 1340, 1315, 1040, 935, 910, 825, 740 cm^{-1}; ms *m/e* 243 (M^+), 215, 199, 174; UV (cyclohexane) 243 nm (ϵ 16 800).

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.01; H, 7.08; N, 5.74.

Thermal and Photochemical Behavior of 2-Phenyl-4-methyl-4-(3-methyl-2-butenyl)-Δ^2-oxazolin-5-one (39). A solution containing 181 mg of **39** in 130 mL of benzene was irradiated under an argon atmosphere for 5 h with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left 140 mg of 2-phenyl-4-methyl-Δ^2-oxazolin-5-one (**41**). The structure of this material was verified by comparison with an authentic sample. Heating a sample of **39** in a 80:20 benzene/pyridine mixture at 155 °C for 16 h gave 2-phenyl-2-(1,1-dimethyl-2-propenyl)-4-methyl-Δ^3-oxazolin-5-one (**40**): NMR ($CDCl_3$, 90 MHz) δ 3.73 (dd, 1 H, J = 16.0, 10.0 Hz), 3.03 (dd, 1 H, J = 16.0, 10.0 Hz).

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Registry No. **9**, 52755-67-6; **10**, 84537-26-8; **11**, 79998-98-4; **12**, 41728-97-6; **13**, 79999-05-6; **14**, 79999-06-7; **15**, 84537-27-9; **16**, 79998-99-5; **18**, 1722-69-6; **19**, 84537-28-0; **21**, 79402-65-6; **22**, 79402-66-7; **23**, 56434-95-8; **25**, 46181-30-0; **25** picrate, 56434-99-2; **26**, 29633-99-6; **27**, 46173-12-0; **27** dimer, 84537-36-0; **28**, 84537-29-1; **29**, 79402-67-8; **30**, 79402-68-9; **31**, 79402-69-0; **32**, 62737-00-2; **33**, 84537-30-4; **34**, 79402-70-3; **35**, 57957-24-1; **36**, 4855-22-5; **37**, 52762-80-8; (±)-**38**, 84620-27-9; (±)-**39**, 84537-31-5; (±)-**40**, 84537-32-6; (±)-**41**, 51127-13-0; 3-methyl-2-phenylazirine, 16205-14-4; *N*-benzoyl-DL-alanine, 1205-02-3; triphenylcyclopropenyl perchlorate, 58003-32-0; diphenylmethylcyclopropenyl perchlorate, 84537-34-8; allyl bromide, 106-95-6; 1-phenyl-3-buten-1-one, 6249-80-5; 2-allyl-2-phenyl-*m*-dithiane, 84537-35-9; 3-methyl-2-butenyl bromide, 870-63-3; 4-methyl-1-phenyl-3-penten-1-one, 36597-09-8; benzonitrile, 100-47-0; methyl bromide, 74-83-9; 2-methyl-4-ethyl-4-phenyl-Δ^2-oxazolin-5-one, 4855-25-8; *N*-(α-ethylbenzylidene)acetamide, 79402-71-4; 2-methyl-4-benzyl-4-phenyl-Δ^2-oxazolin-5-one, 79402-73-6; *N*-(α-benzylbenzylidene)acetamide, 79402-72-5.

Reaction of Phosphorus Pentachloride with 2-Acetylthiophene and Acetophenone

Jacques Kagan,* Sudershan K. Arora, Marius Bryzgis, Som N. Dhawan, Kevin Reid, Shiv P. Singh, and Lucy Tow

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

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The treatment of 2-acetylthiophene with PCl_5, followed by dehydrochlorination, is known to be a poor method for synthesizing 2-ethynylthiophene (**1a**). Reinvestigation of the reaction showed the major products to be the *E* and *Z* isomers of 1,2-dichloro-1-(2-thienyl)ethylene (**7a**), with minor amounts of 1,1-dichloro-1-(2-thienyl)ethane (**3a**), 1-chloro-1-(2-thienyl)ethylene (**4a**), 2-(chloroacetyl)thiophene, and 2-(dichloroacetyl)thiophene. The treatment of acetophenone with PCl_5 yielded similar products, and the mechanism of these reactions is discussed. The major product **7a** could be converted into **1a** by reaction with magnesium. The yield of **4a** was increased when pyridine was also used, when only 1 equiv of PCl_5 was added by portions to the ketone, or when catecholphosphorus trichloride was used instead of PCl_5. The best method for converting 2-acetylthiophene into **1a** goes through the enol phosphonate of 2-(bromoacetyl)thiophene, which is treated with sodium amide.

The treatment of carbonyl compounds with phosphorus pentachloride, followed by double dehydrochlorination of the resulting *gem*-dichloro derivatives, constitutes a classical synthesis of acetylenic compounds.[1,2] Nord and his

$$RCOCH_3 + PCl_5 \rightarrow RCCl_2CH_3 \rightarrow \underset{\mathbf{1}}{RC{\equiv}CH}$$

co-workers applied it to the synthesis of 2-ethynylthiophene (**1a**) from 2-acetylthiophene (**2a**)[3,4] and assumed to have obtained a mixture of 1,1-dichloro-1-(2-thienyl)-ethane (**3a**) and 1-chloro-1-(2-thienyl)ethylene (**4a**), but no pure products were isolated. Their increase in yield from 20–22%[3] to 65%[4] was attributed to the dehydrochlorination procedure. Difficulties with this synthesis were noted,[5] but a full analysis remained to be performed. In this report, the details of the reaction of PCl_5 with **2a** and with the related acetophenone are described, as well as improved methods for obtaining **1a**.

Results and Discussion

The main products of the reaction of **2a** with PCl_5 were analyzed by NMR and by GLC–mass spectroscopy and identified as **3a**, **4a**, **6a**, and **7a** (Scheme I). The major product was **7a** (a mixture of *E* and *Z* isomers accounting for 51% of the isolated products) rather than the expected **3a** and **4a**. Its formation illustrates one danger associated

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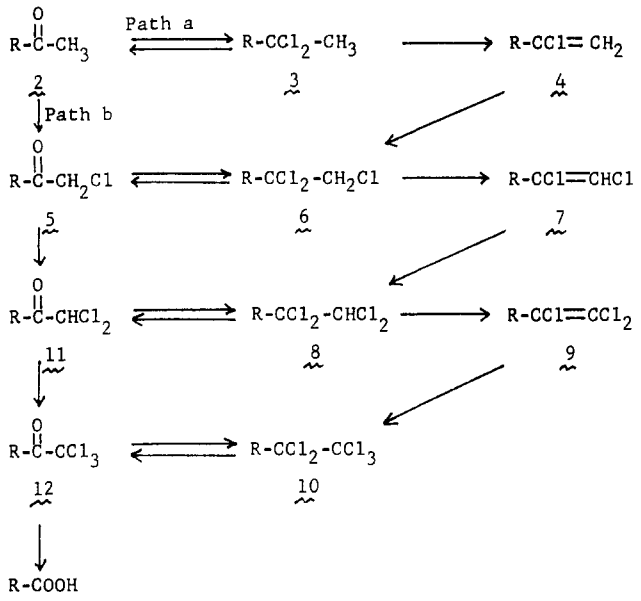
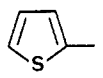
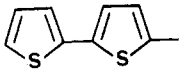
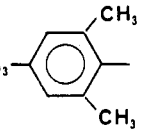
0022-3263/83/1948-0703$01.50/0

Scheme I



a, R = 
b, R = Ph—
c, R = 
d, R = 

with the analysis of reaction products solely on the basis of whether they contain one or two chlorine atoms per molecule.[6] Although the exothermicity of the reaction made the control of the temperature and the obtention of good kinetic data difficult, **4a** appeared to be formed faster than **6a**, itself faster than **7a**, with the concentration of **6a** decreasing as that of **7a** increased.

Known to yield acetylenes directly from certain methyl ketones,[7] the treatment of **2a** with PCl_5 in the presence of pyridine did not produce any **1a**, but it increased significantly the yield of **4a**, from 26% to 50% in the isolated mixtures.

The reaction of acetophenone (**2b**) with PCl_5 was also reinvestigated. Taylor had claimed the formation of only **3b** and **4b**,[8] but neither had been obtained in pure form, and no experimental data supported the contention that they had been formed simultaneously rather than sequentially, as initially proposed.[9] In the presence of 1.1–1.3 equiv of PCl_5, **3b** (33%), **4b** (38%), **5b** (4%), **6b** (8%), **7b** (16%), and **12b** (0.5%) were observed. The trichloro ketone **12b** was isolated in low yield by HPLC, but benzoic acid was obtained instead by column chromatography, resulting from hydrolysis on the support. The compounds **3b** and **6b** were also easily hydrolyzed during chromatography to **2b** and **5b**, respectively.

The presence of an excess of PCl_5 dramatically changed the composition of the products obtained from **2b**. For example, the desired material **4b** was completely absent in the reaction with 2 equiv of PCl_5 in refluxing benzene. A separate treatment of **4b** with 1 equiv of PCl_5 under the same conditions led to its complete disappearance and to the formation (after an aqueous workup) of a mixture of **5b**, **6b**, and a trace of **7b**. This experiment clearly demonstrated that PCl_5 had the ability to act as a chlorinating reagent toward the olefin **4b**, producing **6b** which underwent dehydrochlorination to **7b** and hydrolysis to **5b** during the workup.

It is known that PCl_5 can add to olefins, producing either derivatives having a phosphorus–carbon bond[10] or dichlorinated products.[11] The hypothesis that the former products may be converted into the latter has been advanced,[12] but apparently without rigorous proof. The prior dissociation of PCl_5 into PCl_3 and Cl_2 would also account for the conversion of an olefin into a dichlorinated product, but regardless of the detailed mechanism, one could easily understand the conversion in the presence of PCl_5 of **4**, **7**, and **9** into **6**, **8**, and **10**, respectively. The conversion of **4** into **6** (which could be a source of **5** and **7**) has now been demonstrated directly under the reaction conditions, and the treatment of **7b** with PCl_5 produced a small amount of **8b** (5%), but the formation of the trichloro olefin **9b** was not observed.

The hydrolysis of the gem-dichlorinated products **6**, **8**, and **10** would be expected to produce the α-chloro ketones **5**, **11**, and **12**, respectively, which could also have been formed by stepwise chlorination at the methyl group of **2** (path b in Scheme I). Since **5b** was observed among the reaction products of **2b** in the absence of any aqueous workup, the possibility of converting directly **2b** into **5b** had been demonstrated. However, authentic samples of **5b** and **11b** both failed to lead to further α-chlorination reaction upon treatment with PCl_5.

The major product of the reaction with **5b** was the dichlorostyrene **7b**.[13] This conversion further obscures the origin of **7**, since both pathways a and b can provide this product under the experimental conditions. The treatment of **11b** with PCl_5 did not produce any **12b** and yielded **8b** extremely slowly (less than 12% after 30 h of reflux), probably too slowly to account for the formation of this product in the direct reaction of **2b**.

The reaction of PCl_5 with 5-acetyl-2,2′-bithienyl (**2c**) was reported to give a major product melting at 97-98 °C, with a peak at m/e 248 in the mass spectrum, and a signal at 6.67 ppm in the nmr, supporting the assignment as 5-dichloromethyl-2,2′-bithienyl (13).[14] However, the poor yield of formation of the required precursor **12b** in the case of **2b** and its absence in the case of **2a** suggested that the reaction described by Atkinson et al.[14] required further study.

When the treatment of **2c** with PCl_5 was repeated, the NMR of the crude reaction mixture contained the signal at 6.67 ppm, but the mass spectrum did not show the peak at m/e 248. Preparative TLC led to the isolation of a compound, pure by NMR and melting point, presumed to be identical with that reported.[14] Its mass peak at m/e 260, elemental analysis, and NMR all supported **7c** for the structure of this product.

The observation that an excess of PCl_5 led to undesirable side reactions prompted us to reinvestigate the treatment of **2a** with exactly 1 equiv of PCl_5, adding the reagent in small portions over 30 min to the solution of the ketone. The temperature was maintained at 40–50 °C, and 2 h later all the thiophene protons in the NMR could be accounted

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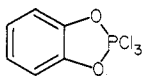
for in terms of a mixture of **2a** (34%), **4a** (27%), **5a** (4%), **6a** (18%), **7a** (12%), and **11a** (5%). This represented a 41% yield of **4a** based on the reacted starting material. An even better yield of **4a** based on converted starting material (67%) was observed in the experiment where pyridine had been added.

From the treatment of **4a** with sodium amide, **1a** could be isolated in 38% yield. The overall yield of conversion of **2a** into **1a** could be much improved by utilizing the major product **7a**, which gave the desired product in 62% upon treatment with magnesium in tetrahydrofuran.

By substituting 14[15,16] for PCl_5, not only was **4a** isolated in 67% yield, based on the reacted starting material, but the dichlorinated product **7a** also was not detected. The overall yield of **1a** from **2a** by this procedure was 25%.



14

Finally, a procedure described for the synthesis of 5-phenyl-2-ethynylthiophene[17] provided a superior method for converting **2a** into **1a**. It consisted in treating the brominated analogue of **5a** (obtained by direct treatment of **2a** with bromine) with triethyl phosphite, followed by sodium amide. The overall yield from **2a** was over 45%.

Conclusion

Even though we did not observe any phenyl- or thienyl-substituted 1,2-dichloroethanes, such as were reported in the treatment of aliphatic ketones with PCl_5,[18] the variety of chlorinated products observed in this work during the reactions of PCl_5 with methyl ketones can easily account for the disappointing yields of acetylenic products which were reported in the literature even when the chlorination with PCl_5 had proceeded in high yield. The relative rates of four processes are particularly important. These are (a) the conversion of the starting material into the *gem*-dichloro compound **3**, (b) the conversion of the starting material into the α-chloro ketone **5**, (c) the polymerization of the intermediate **4**, and (d) its chlorination to give **6**. For reasons which are not obvious to us, the overall balance is more favorable to the synthesis of the acetylenic product in the case of acetophenone than in that of acetylthiophene.

Experimental Section[19]

Reaction of 2-Acetylthiophene with PCl_5 under Nord's Conditions. To 8.25 g (0.0395 mol) of PCl_5, covered with 5.0 mL of dry thiophene-free benzene, was added 3.75 g (0.0297 mol) of 2-acetylthiophene, and stirring was started. Within 5–10 min the mixture darkened, the temperature rose to 40–45 °C, and HCl was evolved. The reaction subsided after about 15 min, and the temperature began to fall. The mixture was then heated on a steam bath to 60–70 °C for 2 h, cooled, and poured slowly over crushed ice. It was extracted with $CHCl_3$ (3 × 100 mL), and the organic layer was washed with water, dried over $MgSO_4$, and concentrated. The NMR spectrum ($CDCl_3$) of the residue (3.96 g) showed signals at δ 2.53 (s), 2.6 (s), 4.24 (s), 4.45 (s), 5.45 (d, J = 2 Hz), 5.68 (d, J = 2 Hz), 6.45 (s), 6.53 (s), and 6.72 (s), in addition to the ring protons at δ 6.87–7.16 (m) and 7.18–7.73 (m). GC/MS analysis of this mixture revealed the following components: **4a**, m/e 144/146 (M^+); **6a**, m/e 214 (with isotopic peaks at m/e 216, 218, 220, M^+), 178 (with isotopic peaks at 180 and 182), 143 and 145, 108; **7a**, *E* and *Z* isomers (ratio 1:2), m/e 178 (with isotopic peaks at 180 and 182, M^+), 143 and 145, 108. From the integration of the NMR signals, the mixture consisted of **2a** (4%), **3a** (5%), **4a** (26%), **6a** (2%), **7a** (51%), and **11a** (11%). Distillation (0.15 torr) afforded samples of the major component **4a** (0.94 g, 8.7%; bp 43–47 °C) and **7a** (1.92 g, 27.3%; bp 55–60 °C).

Dehydrohalogenation of the Crude Reaction Mixture with Sodium Amide in Liquid Ammonia. To a well-stirred solution of sodium amide prepared from 2.3 g (0.1 mol) of freshly cut sodium, 200 mL of liquid ammonia, and a few crystals of $Fe(NO_3)_3$ was added slowly over 25–30 min a solution of 3.25 g of the above crude reaction mixture in 20 mL of absolute ether. A few drops of aniline were then added. The stirring was continued for another 2 h, ammonia was allowed to evaporate, and the residue was decomposed by careful addition of 50 mL of a saturated solution of NH_4Cl. The resulting brown-black mixture was extracted with CH_2Cl_2 (3 × 50 mL), the organic layer was washed with ice–water and with 1 N HCl, was dried over $MgSO_4$, and was concentrated, yielding 2.1 g of residue, which was distilled to afford **1a**: 225 mg (8% based upon **2a**); bp 35 °C (15–17 torr); IR ($CHCl_3$) 2305 cm^{-1}; NMR ($CDCl_3$) δ 3.2 (s, 1 H), 6.8–7.0 (m, 1 H), 7.1–7.3 (m, 2 H).

Reaction of 2-Acetylthiophene (2a) with PCl_5 in the Presence of Pyridine. A mixture of 2.29 g (11 mmol) of PCl_5, 20 mL of dry thiophene-free benzene, and 8 mL of dry pyridine was warmed to 40 °C, and 1.26 g (10 mmol) of 2-acetylthiophene (**2a**) in 5 mL of pyridine was added in one portion. After being refluxed for 2 h, the mixture was worked up in the usual manner. The NMR of residue (2.3 g) revealed the presence of **2a** (25%), **4a** (50%), and **7a** (25%) with no trace of **1a**.

Reaction of Acetophenone (2b) with PCl_5. To a solution of 7.13 g (0.0594 mole) of **2b** in 20.0 mL of thiophene-free dry benzene kept at 65–80 °C was added 16.51 g (0.0792 mol) of PCl_5 in small portions over 20 min. The mixture was stirred at the same temperature for 2 h, chilled, and hydrolyzed by careful addition of 20 g of crushed ice. The cold benzene layer was quickly washed with two 20-mL portions of water, dried immediately over $MgSO_4$, and concentrated under vacuum without heating to afford 9.8 g of a residue with NMR signals ($CDCl_3$) at δ 2.35 (s), 4.23 (s), 4.60 (s), 5.50 (d, J = 2 Hz), 5.70 (d, J = 2 Hz), 6.43 (s), 6.73 (s), and 7.25–7.66 (m). The various components of the mixture were separated by a combination of HPLC with hexane/ethyl acetate (9:1) and preparative TLC with hexane/benzene (5:1) (R_f: **3b**, 0.78; **4b**, 0.80; **5b**, 0.60; **7b**, 0.75; **12b**, 0.15) and identified by comparison of the NMR and mass spectra with those of authentic samples. By NMR integration, the mixture was found to consist of **3b** (33%), **4b** (35%), **5b** (4%), **6b** (8%), **7b** (16%), and a trace of **12b** (0.5%).

Reaction of 2b with 2 Equiv of PCl_5. The procedure described above was followed exactly with 240 mg (2.0 mmol) of **2b** and 834 mg (4.0 mmol) of PCl_5. The NMR of the reaction mixture (300 mg) revealed the presence of **3b** (15%), **5b** (5%), **6b** (25%), and **7b** (50%), while **4b** was absent.

Reaction of Phenacyl Chloride (5b) with PCl_5. Phenacyl chloride (**5b**; 309 mg, 2.0 mmol) was allowed to react with 460 mg (2.21 mmol) of PCl_5 at 0–20 °C as described just above. NMR analysis of the resulting mixture (350 mg) showed the presence of **6b** (57%), *E* and *Z* isomers of **7b** (15%), and unreacted **5b** (28%). When 3 mmol of PCl_5 was used, the crude reaction mixture contained 30% of **6b** and 70% of the *E* and *Z* isomers of **7b**.

Reaction of 2-(Chloroacetyl)thiophene (5a) with PCl_5. 2-(Chloroacetyl)thiophene (**5a**; 321 mg, 2.0 mmol) was allowed to react with 460 mg (2.21 mmol) of PCl_5 exactly as above. By NMR integration, the crude mixture (355 mg) was found to contain **6a** (38%) and **7a** (38%), in addition to the unreacted **5a** (24%). When the reaction was repeated with 3 mmol of PCl_5, the crude mixture contained **5a** (25%), **6a** (25%), and **7a** (50%).

Reaction of 1-Chloro-1-phenylethene (4b) with PCl_5. The procedure described above was followed exactly with 277 mg (2 mmol) of **4b** and 460 mg (2.21 mmol) of PCl_5. NMR analysis of

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(19) The NMR spectra were recorded on Varian T-60 and A-60A spectrometers, and the mass spectra on Perkin-Elmer 270 or AEI MS-30 instruments. The GLC separations took place on 4-ft columns of 20% SE-30 on Chromosorb. A Glenco apparatus with Merck Lobar columns was used for the HPLC separations. Merck 30–70-mesh silica gel was used for column chromatography. The elemental analyses were performed by Micro-Tech Laboratories, Skokie, IL.

the crude reaction mixture (400 mg) indicated the presence of **5b** (40%), **6b** (56%), and **7b** (4%).

Reaction of 1-Chloro-1-(2-thienyl)ethene (4a) with PCl_5. The procedure described above was followed exactly with 290 mg (2.0 mmol) of **4a** and 460 mg (2.21 mmol) of PCl_5. NMR analysis of the crude reaction mixture (390 mg) showed the presence of **5a** (22.5%), **6a** (55%), and **7a** (22.5%).

Reaction of 1,2-Dichloro-1-phenylethene (7b) with PCl_5. The treatment of 346 mg (2.0 mmol) of **7b** with 460 mg (2.21 mmol) of PCl_5 under the conditions described above afforded 330 mg of a residue analyzed by NMR ($CDCl_3$) to be mainly the starting material **7b** with ca. 5% of **8b**, identified by its singlet at 6.05 ppm. A solution of **7b** (340 mg, 2.0 mmol) and PCl_5 (460 mg, 2.21 mmol) in 20 mL of benzene was refluxed for 15 h, 460 mg of PCl_5 was added, and the reflux was continued 15 h longer. After the usual workup, the NMR ($CDCl_3$) of the residue (380 mg) showed that only **7b** (*E* and *Z* isomers, 55%) and **8b** (45%) were present, with no trace of **9b**. These products were separated by preparative TLC (hexane/benzene, 5:1), although most of **8b** became hydrolyzed to **11b** during the separation. A pure sample of **8b** had the following NMR ($CDCl_3$) δ 7.2–8.0 (m, 5 H), 6.05 (s, 1 H); mass spectrum, *m/e* 242 (M^+, with isotopic peaks at 244, 246, 248 and 250), 207 (with 209, 211 and 213), 135 and 137, 77.

Reaction of 1,1-Dichloroacetophenone (11b) with PCl_5. The treatment of 378 mg (2.0 mmol) of **11b** with 460 mg (2.21 mmol) of PCl_5 at 0–20 °C as described with **4b** afforded a residue (360 mg) which was pure starting material from NMR. When a solution of **11b** (378 mg, 2.0 mmol) and PCl_5 (460 mg, 2.2 mmol) in 20 mL of benzene was refluxed for a total of 25 h (with an additional 460 mg of PCl_5 added after 15 h), the NMR ($CDCl_3$) of the residue (350 mg) indicated a mixture of **11b** (88%, singlet at δ 6.80) and **8b** (12%, singlet at δ 6.05); **9b** and **12b** were not detected.

Reaction of 2b with PCl_5 at 0–20 °C. To a stirred solution of 240 mg (2.0 mmol) of **2b** in 20.0 mL of thiophene-free dry benzene was added 460 mg (2.21 mmol) of PCl_5 in small portions over 20 min, keeping the temperature between 0 and 20 °C. After the mixture was stirred at the same temperature for another 2 h, the solvent was evaporated under vacuum at room temperature. The NMR of the crude reaction mixture revealed the presence of **3b** (24%), **4b** (10%), and **5b** (10%) in addition to the unreacted **2b** (54%). After an aqueous workup of the above reaction mixture (290 mg), the products were found to be **2b** (80%), **4b** (10%), and **5b** (10%) by NMR analysis.

Reaction of 2-Acetylthiophene (2a) with 1 Equiv of PCl_5. To a solution of 1.26 g (10 mmol) of **2a** in 20 mL of thiophene-free dry benzene was added 2.08 g (10 mmol) of PCl_5 in small portions over 30 min, keeping the temperature at 40–50 °C. The mixture was then stirred at the same temperature for 2 h, cooled in ice, and carefully hydrolyzed with 2.0 g of crushed ice. The cold benzene layer was quickly washed with water (2 × 20 mL), dried immediately over $MgSO_4$, and concentrated under reduced pressure without heating to afford 1.45 g of a residue: NMR ($CDCl_3$) δ 2.53 (s), 4.24 (s), 4.57 (s), 5.45 (d, J = 2 Hz), 5.68 (d, J = 2 Hz), 6.33 (s), 6.53 (s), 6.72 (s), 6.8–7.4 (m), 7.5–7.8 (m). Integration of these signals revealed that the mixture consisted of **2a** (34%), **4a** (27%), **5a** (4%), **6a** (18%), **7a** (12%), and **11a** (5%).

Reaction of 5-Acetyl-2,2-bithienyl (1c) with PCl_5. A mixture of **1c** (250 mg, 1.20 mmol) and PCl_5 (370 mg, 1.77 mmol) was refluxed for 2.5 h. The cooled solution was poured slowly over crushed ice and was extracted with ether (3 × 20 mL). The ether phase was washed with $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue had NMR signals at δ 2.50 (s), 6.3 (s), 6.67 (s), and 6.90–7.53 (m), corresponding to **2c** (25%) and **7c** (75%, *E* and *Z* isomers which were in the ratio 2:1). The two isomers of **7c** were separated by preparative TLC (hexane–benzene, 5:1). The isomer which was formed in higher yield had the following: mp 98 °C; NMR ($CDCl_3$) δ 6.67 (s, 1 H), 7.0–7.4 (m, 5 H). Anal. Calcd for $C_{10}H_6Cl_2S_2$: C, 45.97; H, 2.30; S, 24.52. Found: C, 45.83; H, 2.31; S, 24.58.

Reaction of 2-Acetylthiophene (2a) with Catechol-phosphorus Trichloride (14). A mixture of 9.0 g (0.0367 mmol) of **14** and 4.6 g (0.0365 mol) of **2a** in 150 mL of dry thiophene-free benzene was refluxed for 3 h. After the mixture was cooled to 15 °C, cold water (100 mL) and diethyl ether (10 mL), followed by 9.0 g of NaOH, were added. The organic layer was washed with brine solution (3 × 50 mL), dried, and concentrated under reduced pressure. The residue was chromatographed over a column of silica gel. Elution with hexane gave 3.5 g (67%) of **4a**.

Dehydrohalogenation of 1-Chloro-1-(2-thienyl)ethylene (4a) with Sodamide. A solution of 3.5 g (0.024 mol) of **4a** in 50.0 mL of dry ether was added in one portion to $NaNH_2$ prepared from 3.5 g of Na in 200 mL of liquid NH_3 and 0.1 g of $Fe_2(NO_3)_3$ at −78 °C. The resulting gray solution was stirred for 3 h at the same temperature and then left at room temperature overnight. The flask was cooled to 0 °C, and 150 mL of water and 200 mL of ether were added. The organic layer was washed with brine solution (3 × 50 mL), dried, and concentrated. Distillation of the residue gave 1.0 g (57%) of **1a**: bp 35 °C (15–17 torr); NMR (CCl_4) δ 3.2 (s, 1 H), 6.8–7.0 (m, 1 H), 7.1–7.3 (m, 2 H).

Dehalogenation of 1,2-Dichloro-1-(2-thienyl)ethylene (7a) with Magnesium. A 2-mL portion of a solution of 895 mg (5.0 mmol) of **7a** in anhydrous THF (20.0 mL) was added to 0.5 g of magnesium turnings and 20.0 mL of anhydrous THF. A crystal of I_2 was added and the mixture warmed until the color disappeared. The remainder of the solution of **7a** was added dropwise over 30 min. The mixture was refluxed for 24 h, cooled, diluted with water, and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated under vacuum, yielding 380 mg of residue which was distilled to afford 340 mg (62% based upon **7a**) of 2-ethynylthiophene (**1a**): bp 35 °C (15-17 torr); IR ($CHCl_3$) 2305 cm^{-1}; NMR ($CDCl_3$) δ 3.2 (s, 1 H), 6.8–7.0 (m, 1 H), 7.1–7.3 (m, 2 H).

Synthesis of 2-Ethynylthiophene (1a) from 2-(Bromoacetyl)thiophene. A mixture of 2-(bromoacetyl)thiophene (6.1 g, 0.03 mol) and triethyl phosphite (15 mL, 0.09 mol) was heated at 90 °C for 1.5 h with stirring under N_2. The excess of triethyl phosphite was removed under vacuum, and the residue, dissolved in 75 mL of ether, was added over a period of 30 min to a stirred suspension of sodamide (prepared from 3.35 g, 0.15 mol, of Na) in 250 mL of anhydrous liquid NH_3 at −78 °C. The mixture was stirred for 1 h at this temperature, NH_4Cl was added, and the NH_3 was allowed to evaporate in a stream of N_2. The residue was poured into water. The combined extract with ether (4 × 50 mL) was dried over $MgSO_4$ and concentrated under vacuum. The residue was distilled to produce 2.44 g (76%) of **1a**: bp 46–46.5 °C (15 torr) [lit.[5] bp 54–60 °C (20 torr)]; NMR ($CDCl_3$) δ 3.3 (s, 1 H), 6.94 (dd, 1 H), 7.20 (m, 2 H).

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Registry No. **1a**, 4298-52-6; **2a**, 88-15-3; **2b**, 98-86-2; **2c**, 3515-18-2; **3a**, 73642-93-0; **3b**, 3141-41-1; **4a**, 84370-27-4; **4b**, 618-34-8; **5a**, 29683-77-0; **5b**, 532-27-4; **6a**, 84370-28-5; **6b**, 19676-38-1; (*E*)-**7a**, 84370-29-6; (*Z*)-**7a**, 84370-30-9; (*E*)-**7b**, 58696-38-1; (*Z*)-**7b**, 58723-96-9; (*E*)-**7c**, 84370-31-0; (*Z*)-**7c**, 84370-32-1; **8b**, 19676-39-2; **9b**, 700-60-7; **11a**, 35304-56-4; **11b**, 2648-61-5; **12b**, 2902-69-4; **14**, 2007-97-8; PCl_5, 10026-13-8; 2-(bromoacetyl)thiophene, 10531-41-6.