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Oxidations by Thionyl Chloride. 8. A Convenient Synthesis of Benzo[*b*]thiophenes from Carboxylic Acids and Ketones[1,2]

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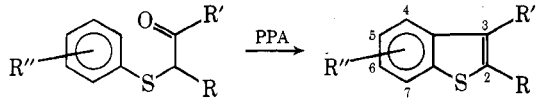
Benzo[*b*]thiophenes are prepared in one step from cinnamic acids, hydrocinnamic acids, or certain ketones plus thionyl chloride and pyridine. Para-substituted cinnamic acids gave rise to benzo[*b*]thiophenes in 41–69% yields together with α-chlorocinnamic acid derivatives. 3-Substituted 3-phenylpropanoic acids gave 3-aryl- or -alkyl benzo[*b*]thiophenes in 77% (3-H) to 16% (3-CH_3) yield; in the latter case, uncyclized sulfenyl chloride was also found. Ketones of the type $PhCH_2CH_2COR$ gave benzo[*b*]thiophenes in 52% (R = Ph) and 68% (R = *tert*-butyl) yields. An alternative two-step synthesis from 3-substituted 3-phenylpropanoic acids via cyclization of sulfenyl chloride **11** furnished benzo[*b*]thiophenes in 61% (3-H) and 66% (3-CH_3) yields, but only 2-chloro-1-phenylinden-3-one (**13**) and 1-oxoindeno[2,3-*d*]benzo[*b*]thiophene (**14**) in 12 and 63% yields, respectively (3-Ph). The indenones were also prepared by Friedel–Crafts cyclization of the sulfenyl chlorides derived from cinnamic acids.

Among a number of synthetic methods known[3,4] for the preparation of benzo[*b*]thiophenes, cyclodehydration of aryl sulfides (for example, arylthio acetones, eq 1) is the most



(1)

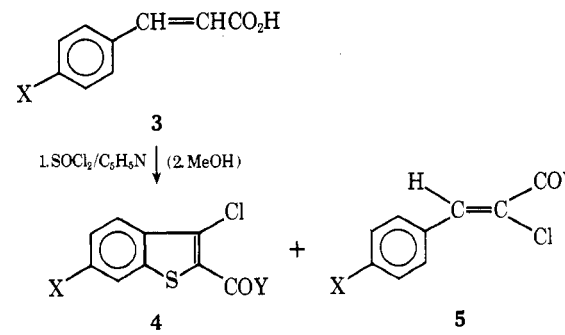
1 2

common and widely practiced method. This method unambiguously affords 5- and 7-substituted benzo[*b*]thiophenes from para- and ortho-substituted phenyl sulfides, respectively, but mixtures of 4- and 6-substituted benzo[*b*]thiophenes result from meta-substituted starting materials. In this method, preparation of starting materials usually requires a several-step sequence of reactions.

On the other hand, as evident from a previous paper,[5] if the reaction of thionyl chloride with cinnamic acids or 3-arylpropanoic acids can be generally applied, it would furnish 4- and 6-substituted benzo[*b*]thiophenes from ortho- and para-substituted starting materials, respectively, and 5- and 7-substituted benzo[*b*]thiophenes from meta-substituted starting materials. Thus the reaction would offer a convenient method for the preparation of benzo[*b*]thiophenes not only by supplementing the cyclodehydration methods, but also by being a one-step synthesis. We now describe a synthetic application of the thionyl chloride reaction to the preparation of benzo[*b*]thiophenes.[6]

Results and Discussion

Direct Synthesis of Benzo[*b*]thiophenes from Cinnamic Acids, 3-Phenylpropanoic Acids, and Certain 3-Phenyl 1-Substituted 2-Propanones. As described in a preceding paper,[5] cinnamic acid (**3a**) furnished the benzo[*b*]-thiophene **4a** in 69% yield when treated with an excess of thionyl chloride and a catalytic amount of pyridine at 120–125 °C.

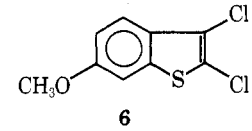


Yield of 4, %

a, X = H; Y = Cl	69
b, X = CH_3; Y = Cl	60.7
c, X = CH_3; Y = OCH_3	40.5
d, X = OCH_3; Y = OCH_3	47.5
e, X = NO_2; Y = OCH_3	46

Similarly *p*-methylcinnamic acid (**3b**) gave benzo[*b*]thiophene **4b** in 60.7% yield and the methyl ester **4c** in 40.5% yield. *p*-Methoxy- (**3d**) and *p*-nitrocinnamic acids (**3e**) furnished benzo[*b*]thiophenes **4d** and **4e** in 47.5 and 46% yield, respectively. The structures of **4a–e** were assigned by spectroscopic data and elemental analyses. No attempt was made to maximize the yields of these products.

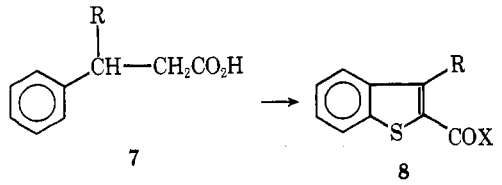
Common by-products for the reactions of the acid **3a** to **3d** were α-chlorocinnamic acid derivatives **5**. The reaction of **3e** did not give **5e**, but methyl α,β-dichloro-4-nitrocinnamate and methyl 4-nitrobenzoate as minor products. Another minor product from the reaction of **3d** was the benzo[*b*]thiophene **6** which, isolated in 0.7% yield, showed no carbonyl absorption



6

in the infrared spectrum. The mass spectrum [*m/e* 232 (100), 234 (68.5), 236 (15.7%)] indicated the presence of two chlorine atoms. Thus the structure was assigned as indicated by analogy to other 2,3-dichlorobenzo[*b*]thiophenes[5] isolated from the reaction of other cinnamic acids.

The reaction of 3-phenylpropanoic acid (**7a**) previously afforded the benzo[*b*]thiophene **4a** in 31.6% yield.[7] The yield of **4a** was improved to 77% when **7a** was treated with 5 equiv of thionyl chloride and 0.12 equiv of pyridine at 140–150 °C for 6 h. Under similar conditions 3,3-diphenylpropanoic acid (**7b**) gave after hydrolysis the known[8] benzo[*b*]thiophene **8b** in 65% yield.

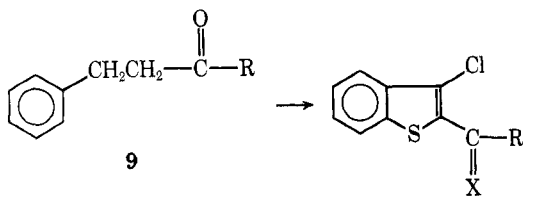


7 **8**

a, R = H; X = OH
b, R = C_6H_5; X = OH
c, R = CH_3; X = Cl
d, R = CH_3; X = OCH_3

The reaction of 3-phenylbutanoic acid **7c**, however, furnished the corresponding benzo[*b*]thiophene **8c** in only 16% yield. Prolonged heating did not improve the yield. Most of the material remained as uncyclized sulfenyl chloride. This slow cyclization was an important clue to the cyclization mechanism.[5] These two examples show that 3-alkyl or aryl substituted benzo[*b*]thiophenes can be prepared by a one-step reaction from 3-phenylpropanoic acids. In contrast, a previous synthesis of **8b** required several steps.[8]

Apart from carboxylic acids, ketones of the type Ar-$CHRCH_2COR'$, in which the R′ group has no enolizable hydrogens, can also form benzo[*b*]thiophenes when treated with an excess of thionyl chloride and a catalytic amount of pyridine. We examined the reaction with two such ketones, benzylacetophenone (**9a**) and benzylpinacolone (**9b**). Thus treatment of **9a** with 3 equiv of thionyl chloride and a catalytic amount of pyridine at 125–130 °C for 3 h furnished, after separation on an alumina column, the benzo[*b*]thiophene **10a**



9 **10**

	Yield, %
a, R = C_6H_5; X = O	52
b, R = $C(CH_3)_3$; X = O	53.5
c, R = $C(CH_3)_3$; X = Cl_2	14.3

in 52% yield. Similarly, treatment of **9b** with 4 equiv of thionyl chloride afforded the benzo[*b*]thiophenes **10b** and **10c** in 53.5 and 14.3% yield, respectively.

The structure of **10a** was assigned by elemental analysis and spectroscopic data: the NMR spectrum showed only aromatic hydrogens at δ 7.92 and 7.55 (multiplets); the infrared spectrum revealed carbonyl absorption at 1634 cm^{-1}, a position which is virtually identical with that (1631 cm^{-1}) reported[9] for 2-benzoylbenzo[*b*]thiophene; and the mass spectral fragmentation pattern correlated well with that of **4a**.

The structure of **10b** was assigned by analogy to **10a**. Compound **10c** showed no carbonyl absorption in the ir spectrum, but the NMR spectrum [δ 7.95–7.32 (m, 4 H), 1.36 (s, 9 H)] was almost identical with that [δ 7.96–7.34 (m, 4 H), 1.33 (s, 9 H)] of **10b**. Furthermore, **10c** was obtained in 15.5% yield by independent treatment of **10b** with thionyl chloride and pyridine at 130 °c for 1 h. Indeed, some examples of such chlorination of ketones by thionyl chloride to form *gem*-dichlorides are known,[10] and the reaction appears to be especially facile in the presence of a tertiary amine.

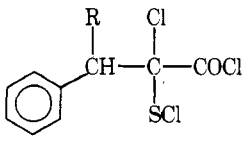
The yields of benzo[*b*]thiophenes obtained from ketones in the above examples are moderate and comparable to those of benzo[*b*]thiophenes obtained from cinnamic acids and 3-phenylpropanoic acids. Unfortunately, however, with the exception of **8b** and **8c**, the benzo[*b*]thiophenes thus far obtained have been those possessing a chlorine substituent at the 3 position. Because this constitutes a limit on the scope of our synthesis, we developed a method that has more general applicability to the synthesis of benzo[*b*]thiophenes.

Synthesis of Benzo[*b*]thiophenes by Friedel–Crafts Reaction of Sulfenyl Chlorides. Alkyl sulfenyl chlorides, when treated with aromatic compounds and aluminum chloride, are known[11] to afford aryl alkyl sulfides. Thus it was proposed that application of the reaction to a sulfenyl chloride such as **11** would effect, intramolecularly, the formation of benzo[*b*]thiophenes which have no chlorine substituent at the 3 position.

Sulfenyl chlorides of the type **11** can be easily prepared by treating carboxylic acids **7** with thionyl chloride and pyridine. Typically the α-methylene group of a saturated carboxylic acid is completely oxidized by treatment of the acid with 7 equiv of thionyl chloride and 0.12 equiv of pyridine at reflux (bath temperature 95 °C) for 21 h. The product mixture, after excess thionyl chloride and pyridine hydrochloride are removed, usually consists of approximately 80% sulfenyl chloride which can be used for cyclization without further purification.

Thus, sulfenyl chloride **11a**, prepared from **7a**, was treated with 1 equiv of aluminum chloride in methylene chloride at 5–10 °C and hydrolyzed to yield benzo[*b*]thiophene-2-carboxylic acid (**8a**) in 61– yield. Similarly sulfenyl chloride **11c**, prepared from **7c**, was treated with 2.2 equiv of aluminum chloride in methylene chloride at 0–3 °C, esterified with methanol, and separated by column chromatography to furnish the known[12] benzo[*b*]thiophene **8d** in 66% yield. Thus the yield was improved by 50% from the direct method.

Sulfenyl chloride **11c** was shown to be a 1:1 mixture of di-

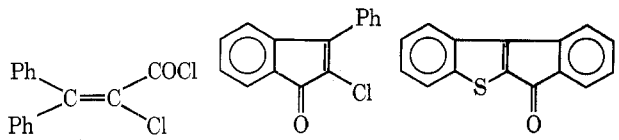


11a, R = H
b, R = C_6H_5
c, R = CH_3
d, R = Cl

astereomers by NMR spectroscopy [δ 7.28 (m, aromatic), 4.02 and 3.91 (two sets of q, methine), 1.58 and 1.47 (two sets of d, methyl protons)].

Treatment of **7b** with thionyl chloride and pyridine under the conditions for forming sulfenyl chloride furnished a mixture which was composed of 72% of **11b** and 28% of a mixture assumed to be the olefin **12** and the acid chloride of **8b**. Treatment of the entire mixture with an excess of aluminum chloride in methylene chloride at 0–3 °C afforded a red solid mixture which upon separation on an alumina column furnished the known[13] indenones **13** as orange and **14** as red crystals in 12 and 63% yield, respectively. Indenone **13** would presumably be formed by cyclization of **12**, while **14** would be

formed by cyclization of both **11b** and the acid chloride of **8b**.



12 **13** **14**

Compounds **13** (33%) and **14** (35%) were also obtained by Friedel–Crafts reaction on the mixture formed when β-phenylcinnamic acid was treated with thionyl chloride and pyridine. Another example which unexpectedly produced **14** was the Friedel–Crafts reaction of sulfenyl chloride **11d** with benzene. Thus treatment of **11d**, prepared[5] from cinnamic acid, with 2.2 equiv of aluminum chloride in benzene at 10–15 °C afforded, after separation on an alumina column, **14** in 42% yield.

Such application of Friedel–Crafts reactions on sulfenyl chlorides as shown by the above examples makes the reaction of thionyl chloride a more useful and general method for the synthesis of benzo[b]thiophenes than direct formation of the compounds. Furthermore, certain indenones may also be prepared. This is just another example of sulfenyl chlorides, prepared by the oxidation of carboxylic acids or certain ketones with thionyl chloride, having high potential as synthetic intermediates.

Experimental Section

Thionyl chloride (Matheson Coleman and Bell) was distilled from triphenyl phosphite;[15] the fraction boiling over the range 75.5–76.5 °C was used. Alumina used for chromatographic columns was Woelm neutral unless otherwise specified. Infrared spectra were recorded with a Perkin-Elmer Model 137 spectrophotometer with a sodium chloride prism; solid samples were taken as potassium bromide pellets and liquid samples were taken as neat films. Mass spectra were processed by Mr. C. R. Weissenberger with an AEI MS-9 mass spectrometer[16] at 70 eV. The nuclear magnetic resonance spectra were taken on a Varian Model A-60 spectrometer, using tetramethylsilane as the internal reference and carbon tetrachloride as solvent unless otherwise specified. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are corrected. Boiling points are uncorrected. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., and Galbraith Laboratories, Knoxville, Tenn.

General Procedure for the Reaction of Thionyl Chloride with Para-Substituted Cinnamic Acids. To a mixture of 0.02 mol of a para-substituted cinnamic acid and 0.2 ml of pyridine was added one-third of 8.4 g (0.07 mol) of thionyl chloride; the mixture then was heated to 140 °C. The rest of the thionyl chloride was added at such a rate that the temperature did not drop below 135 °C. The mixture was heated at the same temperature for an additional 30 min, cooled, esterified with excess methanol and benzene, and separated on an alumina column.

3-Chloro-2-chlorocarbonyl-6-methylbenzo[b]thiophene (4b). *p*-Methylcinnamic acid (**3b**, 8.10 g, 0.05 mol) was treated with 21.0 g (0.175 mol) of thionyl chloride and 0.5 ml of pyridine under the conditions of the general procedure. The mixture (acid chlorides) was dissolved in hot hexanes (300 ml) and decanted to separate pyridine hydrochloride. Four recrystallizations from the solution afforded 7.11 g of **4b**, mp 123.5–125.7 °C. The residue was distilled to yield 3.30 g of yellow oil, bp 93–100 °C (0.3–0.4 mm), and undistilled material which upon recrystallization from hexanes furnished 0.33 g of **4b**. Thus the total yield of **4b** was 7.44 g (60.7%). A pure sample of **4b** appeared as pale yellow needles: mp 124.7–125.7 °C; ir 5.67 (C=O), 6.25 (C=C), 6.80, 8.54, 10.96, 12.29, and 14.04 μ; mass spectrum *m/e* 246, 244 (M^+), 211, 209 (base, - Cl), and 181 (- COCl).

The distillate was a mixture of *p*-methylcinnamoyl chloride (10%) and α-chloro-*p*-methylcinnamoyl chloride (**5b**, 23%) as shown by NMR spectroscopy after esterification with methanol.

3-Chloro-2-methoxycarbonyl-6-methylbenzo[b]thiophene (4c). *p*-Methylcinnamic acid (**3b**, 3.24 g, 0.02 mol) was treated with thionyl chloride and pyridine and then with absolute methanol (70 ml) and benzene (30 ml) under the conditions of the general procedure. The product was separated on a column (100 g of activity grade II alumina) by eluting with petroleum ether into 23 fractions (50–100 ml each) and petroleum ether–ether (5:1) into 3 fractions (150 ml each). Fractions 1–3 gave approximately 0.1 g of sulfur. The material obtained by combining fractions 4–23 (total 3.55 g) was recrystallized from ligroin to furnish 1.85 g of **4c**, mp 84.5–89 °C. The residue after separation of **4c** was distilled to yield 1.00 g of a mixture (2:3) of methyl *p*-methylcinnamate and methyl α-chloro-*p*-methylcinnamate. The mixture was confirmed by the comparison of the NMR spectrum with those of authentic samples. The distillation residue was crystallized from ligroin to yield 0.1 g more of **4c**, mp 84–88 °C. Thus the total yield of **4c** was 1.95 g (40.5%). Further recrystallization from ligroin afforded an analytical sample of **4c** as white plates: mp 88.5–89 °C; NMR ca. δ 7.79 (d, H_4, J = 8.5 Hz), 7.45 (finely splitted singlet, H_7), 7.16 (finely splitted doublet, H_5, J = 8.5 Hz), 3.89 (s, OCH_3), and 2.45 (s, CH_3); ir 5.93 (C=O), 6.70, 7.67, 7.86, 8.06 (C–O), and 9.20 μ; mass spectrum *m/e* 242, 240 (M^+), 211, 209 (base, $-OCH_3$), 181 ($-CO_2CH_3$), and 145 ($-CO_2CH_3$, –HCl).

Anal. Calcd for $C_{11}H_9ClO_2S$: C, 54.89; H, 3.77; Cl, 14.73; S, 13.32. Found: C, 54.73; H, 3.51; Cl, 14.96; S, 13.31.

3-Chloro-6-methoxy-2-methoxycarbonylbenzo[b]thiophene (4d). *p*-Methoxycinnamic acid (**3d**, 3.56 g, 0.02 mol) was treated with thionyl chloride and pyridine, followed by methanol (100 ml) and benzene (40 ml) under the conditions of the general procedure. The product was separated on a column (150 g of activity grade III alumina) by eluting with petroleum ether–benzene (1:1) into 13 fractions (50 ml each). Fractions 3–6 (3.57 g) were mixtures which were combined and fractionally crystallized from ethanol to furnish 2.185 g (42.5%) of **4d**, mp 131–138 °C, and 0.92 g (20%) of **5d**, mp 65–70 °C.

The latter compound was recrystallized from ethanol–water to afford white, fine crystals: mp 67–70 °C; NMR δ 7.70 (s, one vinyl), 7.67 and 6.86 (AB quartet, four aromatic hydrogens, J = 9.0 Hz), and 3.79 and 3.76 (2 s, 2 OCH_3); ir 5.85 (C=O) and 6.23 μ (C=C); mass spectrum *m/e* 228 (M + 2) and 226 (M^+).

An analytical sample of **4d** was obtained by further recrystallization from ethanol, giving white, fine needles: mp 138–138.5 °C; NMR ($CDCl_3$) ca. δ 7.72 (d, H_4, J = 8.5 Hz), 7.13 (d, H_7, J = 2.0 Hz), 7.01 (dd, H_5, J = 8.5, 2.0 Hz), and 3.91 and 3.85 (2 s, 2 OCH_3); ir 5.93 (C=O) and 6.25 μ (C=C); mass spectrum *m/e* 258, 256 (M^+, base), 227, 225 ($-OCH_3$), and 197 ($-CO_2CH_3$).

Anal. Calcd for $C_{11}H_9ClO_3S$: C, 51.47; H, 3.53; Cl, 13.81; S, 12.49. Found: C, 51.26; H, 3.39; Cl, 13.71; S, 12.67.

The compound **4d** was separated in 47.5% yield when the product after esterification was directly crystallized from ethanol.

2,3-Dichloro-6-methoxybenzo[b]thiophene (6). *p*-Methoxycinnamic acid (**3d**) was treated with thionyl chloride and pyridine followed by methanol and benzene under the conditions of the general procedure. Separation of the product was effected on a column (activity grade II alumina) by eluting with petroleum ether into eight fractions (50 ml each). Fractions 4–6 upon recrystallization from 95% ethanol afforded 34 mg (0.7%) of **6**: mp 70–73 °C; ir 6.23 (C=C), 6.78, 7.89 (C–O), and 12.07 μ; mass spectrum *m/e* 236 (M + 4), 234 (M + 2), 232 (M^+, base), 221, 219, 217 ($-CH_3$), 191, and 189 ($-COCH_3$).

3-Chloro-2-methoxycarbonyl-6-nitrobenzo[b]thiophene (4e). Under the conditions of the general procedure *p*-nitrocinnamic acid (**3e**, 3.86 g, 0.02 mol) was treated with thionyl chloride and pyridine, followed by absolute methanol (100 ml). The product was chromatographed on an alumina (activity grade III, 150 g) column by eluting with benzene into 20 fractions (50 ml each for fractions 1–7, 125 ml for 8–12, 250 ml for 13–17, and 500 ml for 18–20). Recrystallization of the fractions 4–20 (2.51 g) from ethyl acetate gave rise to 1.93 g of **4e**, mp 214.5–215.5 °C. Fractions 2 and 3 (1.52 g) were fractionally crystallized to furnish 0.57 g of **4e**, mp 214–215 °C, and 0.88 g of a mixture. Thus the separated yield of **4e** was 2.50 g (46%). Further recrystallization of **4e** from ethyl acetate afforded an analytical sample as yellow prisms: mp 216–216.5 °C; NMR ($CDCl_3$) ca. δ 8.72 (d, H_7, J = 2.0 Hz), 8.29 (dd, H_5, J = 9.0, 2.0 Hz), 8.07 (d, H_4, J = 9.0 Hz), and 4.00 (s, OCH_3); ir 5.93 (C=O) and 8.03 μ (C–O); mass spectrum *m/e* 273, 271 (M^+, base), 241 (–NO), 242, 240 ($-OCH_3$), 196, 194 ($-NO_2$, $-OCH_3$), and 166 ($-NO_2$, $-CO_2CH_3$).

Anal. Calcd for $C_{10}H_6ClNO_4S$: C, 44.21; H, 2.23; Cl, 13.05; N, 5.16; S, 11.80. Found: C, 44.52; H, 2.08; Cl, 13.33; N, 5.18; S, 11.87.

The residue after separation of **4e** from fractions 2 and 3 was sublimed at 60 °C (0.3 mm) for 3 h to yield 0.10 g of methyl *p*-nitrobenzoate: mp 91.5–92.5 °C (lit.[17] 96 °C); NMR δ 8.20 (s, four aromatic) and 3.97 (s, three methyl hydrogens); ir 5.80 (C=O), 6.23, and 7.85 μ; mass spectrum *m/e* 181 (M^+) and 150 (base, $-OCH_3$).

3-Chloro-2-chlorocarbonylbenzo[b]thiophene (4a). To a mixture of 7.5 g (0.05 mol) of **7a** and 0.5 ml of pyridine was added ca. ⅕ of 30 g (0.25 mol) of thionyl chloride. The mixture was heated to 140 °C, and the rest of the thionyl chloride was added at a rate as not to drop the temperature below 135 °C (2 h). The mixture was then

heated at 140–150 °C for an additional 4 h. After cooling, the mixture was dissolved in 200 ml of hot hexane and decanted from pyridine hydrochloride. Crystallization of the solution furnished 8.94 g (77%) of benzo[*b*]thiophene **4a**, mp 114.5–115.5 °C. The remaining material (1.80 g) consisted of **5a** and other unidentified products as shown by NMR spectroscopy.

3-Phenylbenzo[*b*]thiophene-2-carboxylic Acid (8b). To a mixture of 3,3-diphenylpropanoic acid (**7b**, 2.00 g, 0.009 mol) and 0.9 ml of pyridine was added 1 equiv (ca. 0.8 ml) of thionyl chloride. The mixture was heated to 150–160 °C, more thionyl chloride (ca. 2.3 ml, total amount of thionyl chloride was 5.0 g) was added over a period of 1 h, and this mixture was heated at this temperature for an additional 2 h. The product was added dropwise with stirring to a mixture of 10 ml of water, 1 ml of concentrated hydrochloric acid, and 15 ml of tetrahydrofuran, and heated at reflux for 3 h. The tetrahydrofuran was distilled and the residue was cooled, extracted with ether, washed with saturated sodium chloride solution, dried ($MgSO_4$), and concentrated to yield white solid. The solid was crystallized from benzene to yield 1.49 g (65%) of white powder, mp 197–199 °C. Recrystallization from the same solvent gave pure acid **8b**, mp 199–200 °C (lit.[8] mp 199–200 °C).

2-Chlorocarbonyl-3-methylbenzo[*b*]thiophene (8c). To a mixture of 4.11 g (0.025 mol) of **7c** and 0.25 ml of pyridine was added 12.0 g (0.1 mol) of thionyl chloride at 120–130 °C over a period of 2 h. The mixture was heated at this temperature for an additional 6 h. After excess thionyl chloride and pyridine hydrochloride were removed, the resulting black mixture was crystallized from *n*-hexane to yield 0.85 g (16%) of crude **8c**, mp 90–105 °C (lit.[12] mp 108–109 °C), and 0.20 g of sulfur. Most of the remaining material was the sulfenyl chloride **11c** as shown by infrared spectroscopy.

2-Benzoyl-3-chlorobenzo[*b*]thiophene (10a). To a mixture of 2.10 g (0.01 mol) of **9a** and 0.1 ml of pyridine was added 3.6 g (0.03 mol) of thionyl chloride at 125 °C over a period of 30 min. The mixture was heated at 125–130 °C for an additional 2.5 h, cooled, taken up into ether, successively washed with water and with saturated sodium chloride solution, dried ($MgSO_4$), and evaporated to yield 2.70 g of a very viscous oil. The oil was placed on an alumina (activity grade I, 70 g) column and eluted with light petroleum ether–ether (5:1) into ten fractions (100–200 ml each). Fractions 3–7 (950 ml, 1.51 g) were recrystallized from hexane to yield 1.42 g (52%) of the benzo[*b*]thiophene **10a**, mp 77–78 °C. Further recrystallization from hexane afforded an analytical sample: mp 78 °C; NMR δ 7.92 (m) and 7.55 (m); ir 6.12 μ.

Anal. Calcd for $C_{15}H_9ClOS$: C, 66.05; H, 3.33; Cl, 13.00; S, 11.76. Found: C, 65.92; H, 3.34; Cl, 13.01; S, 11.62.

Benzylpinacolone (9b). Benzalpinacolone[18] (18.8 g, 0.01 mol, mp 42–43 °C) was hydrogenated with atmospheric hydrogen over 10% palladium on charcoal (1 g) in 80 ml of ethyl acetate at room temperature till uptake (2450 ml) ceased. After removal of the catalyst and the solvent the product was distilled to yield 18.61 g (97.8%) of benzylpinacolone **9b**: bp 60–62 °C (0.007 mm); ir 3.34 and 5.86 μ (C=O); NMR δ 7.12 (s, 5 H), 2.77 (m, 4 H), and 1.04 (s, 9 H).

Reaction of Thionyl Chloride with Benzylpinacolone (9b). To a mixture of 3.60 g (0.019 mol) of **9b** and 0.19 ml of pyridine was added 9.1 g (0.076 mol) of thionyl chloride at 120–130 °C over a period of 50 min. Approximately three-quarters of the thionyl chloride was rapidly consumed (30 min). The mixture was heated at this temperature for an additional 1 h, cooled, and directly chromatographed on an alumina (activity grade III, 180 g) column. The column was eluted with light petroleum ether into 15 fractions (50 ml each for fractions 1–5 and 100 ml each for 6–15). Recrystallization of fractions 1 and 2 from 95% ethanol afforded 30 mg of sulfur and 835 mg (14.3%) of benzo[*b*]-thiophene **10c**: mp 107–108 °C; ir no carbonyl absorption; NMR δ 7.95–7.32 (m, 4 H) and 1.36 (s, 9 H).

Anal. Calcd for $C_{13}H_{13}Cl_3S$: C, 50.75; H, 4.26; Cl, 34.57; S, 10.42. Found: C, 50.53; H, 4.21; Cl, 34.36; S, 10.57.

The residue of fraction 2 and fractions 3–6 furnished 2.67 g (53.5%) of benzo[*b*]thiophene **10b**: bp 103–107 °C (0.1 mm); ir 3.32 (C–H) and 5.91 μ (C=O); NMR δ 7.96–7.34 (m, 4 H) and 1.33 (s, 9 H); mass spectrum *m/e* 254 (M + 2), 252 (M^+), 197, 195 (–C_4H_9, base), 167 (–COC_4H_9), 132 (–COC_4H_9, –Cl), 123 (–COC_4H_9, –CS), 57 (C_4H_9), and 41 (C_3H_5).

Fractions 7–15 were small amounts of mixtures.

Reaction of Thionyl Chloride with 3-Chloro-2-benzo[*b*]thienyl *tert*-Butyl Ketone (10b). To a mixture of 0.5 g (2 mmol) of **10b** and 3 drops of pyridine was added portionwise at 130 °C 1 g of thionyl chloride. The mixture was heated over a period of 1 h, excess thionyl chloride was removed, and the residue was separated on an alumina (activity grade I, 30 g) column by eluting with petroleum ether into seven fractions (50 ml each). Fractions 2–6 afforded 95 mg (15.5%) of **10c**, mp 104–106 °C. Recrystallization from 95% ethanol gave mp 107–108 °C. The infrared spectrum was identical with that obtained previously.

General Procedure for the Preparation of Sulfenyl Chlorides Used for Friedel–Crafts Reaction. A carboxylic acid was treated with 7 equiv of thionyl chloride and 0.12 equiv of pyridine at moderate reflux (bath temperature 95 °C) for 21 h. After excess thionyl chloride was removed, the product was dissolved in hexane or benzene and filtered to remove pyridine hydrochloride. Solvent was removed by distillation under vacuum, and purity of the sulfenyl chloride was determined by NMR spectroscopy. The sulfenyl chloride was used for cyclization without further purification.

Benzo[*b*]thiophene-2-carboxylic Acid (8a). To a vigorously stirred solution of 5.0 g (0.015 mol) of sulfenyl chloride **11a** (purity 80%) in 150 ml of dry methylene chloride was added portionwise over a 10-min period 2.0 g (0.015 mol) of aluminum chloride (powder). The solution, which turned from yellow to red and then to black, was stirred at 5–10 °C for an additional 1 h and decomposed with 60 ml of 3 N hydrochloric acid. The layers were separated, and the aqueous layer was extracted with methylene chloride (2 × 50 ml). The combined methylene chloride solution was washed with saturated sodium chloride solution and solvent was evaporated to furnish crude 2-chlorocarbonylbenzo[*b*]thiophene. The crude product was hydrolyzed by heating with an ethanol (50 ml)/20% sodium hydroxide (15 ml) solution. After the solution was extracted with ether, the aqueous solution was acidified with 30 ml of 10% hydrochloric acid and extracted with ether (3 × 50 ml). The latter ethereal solution was dried ($CaCl_2$) and evaporated to yield 3.2 g of crude acid which upon crystallization from benzene–ethyl acetate afforded 0.8 g of **8a**, mp 236–238 °C. Second and third crystallizations gave 0.83 g of less pure product, mp 215–230 °C; total yield of **8a** was 1.63 g (61%).

2-Chloro-2-chlorosulfenyl-3-phenylbutanoyl Chloride (11c). Compound **11c**, prepared from 3-phenylbutanoic acid according to the general procedure, was shown to be a mixture (1:1) of diastereomers and 90% pure by NMR spectroscopy: δ 7.28 (m, aromatic), 4.02 and 3.91 (pair of quartets, methine), and 1.58 and 1.47 (pair of doublets, methyl hydrogens). The infrared spectrum of **11c** showed characteristic carbonyl absorptions at 5.60 and 5.70 μ (shoulder).

3-Methyl-2-methoxycarbonylbenzo[*b*]thiophene (8d). To a vigorously stirred solution of 3.3 g (0.0105 mol) of sulfenyl chloride **11c** in 150 ml of dry methylene chloride was added at 1–3 °C over a period of 30 min 3.07 g (0.023 mol) of aluminum chloride (powder). The mixture was stirred at room temperature for another 30 min and then decomposed with 60 ml of 6 N hydrochloric acid. The layers were separated, and the aqueous layer was extracted with methylene chloride (100 ml). The combined methylene chloride solution was dried ($CaCl_2$) and concentrated to yield 2.50 g of crude acid chloride **8c** which was then treated with absolute methanol (100 ml) at reflux for 1 h. A small amount of insoluble tar was separated and discarded. The methanolic solution was concentrated to yield 2.0 g of crude ester **8d**. The crude product was separated on a silica gel (activity grade I, 50 g) column by eluting with 600 ml of petroleum ether–ether (10:1) to furnish 1.43 g (66%) of **8d**, mp 99–102 °C. Recrystallization of this product from ligroin gave slightly yellow needles: mp 102.5–103 °C (lit.[12] mp 101–102 °C); ir 5.89 (C=O), 6.60, 7.01, 7.94, and 8.10 μ (C–O); NMR ($CDCl_3$) δ 7.71 and 7.33 (m, aromatic), 3.86 (s, OCH_3), and 2.68 (s, CH_3).

2-Chloro-2-chlorosulfenyl-3,3-diphenylpropanoyl Chloride (11b). 3,3-Diphenylpropanoic acid (**7b**, mp 154.5–155.5 °C) was treated with thionyl chloride and pyridine under the conditions of the general procedure to furnish a yellow, viscous oil which contained sulfenyl chloride **11b** (72%) and presumably olefin **12** and the acid chloride of **8b** as minor components. The NMR spectrum showed absorptions at δ 7.30 (m) due to aromatic hydrogens of all the components and δ 5.25 (s) due to the methine hydrogen of **11b**.

1-Oxoindeno[2,3-*d*]benzo[*b*]thiophene (14) and 2-Chloro-1-phenylinden-3-one (13). The yellow oil (2.66 g) obtained by treatment of 3,3-diphenylpropanoic acid with thionyl chloride and pyridine was treated with aluminum chloride in methylene chloride under the same conditions described for the preparation of **8d**. The crude product (2.05 g) thus obtained was separated on an alumina (activity grade I, 50 g) column. Elution with 400 ml of petroleum ether–ether (10:1) gave rise to 0.22 g (12%) of **13**. Further elution with 300 ml of benzene furnished 1.16 g (63%, based on **7b**) of **14** as red crystals, mp 185–190 °C. Recrystallization from ligroin–benzene afforded **14** as red needles: mp 194.5–196 °C (lit.[14] 195–196 °C); ir identical with the reported[14] spectrum; NMR ($CDCl_3$) δ 8.03–7.06 (m); mass spectrum *m/e* 237 (M + 1), 236 (M^+, base), and 208 (–CO); mol wt (mass spectrum) for $^{12}C_{15}{}^{1}H_8{}^{16}O^{32}S$ 236.02949 (calcd, 236.02958).

Anal. Calcd for $C_{15}H_8OS$: C, 76.24; H, 3.41; S, 13.56. Found: C, 75.82; H, 3.29; S, 13.44.

Crude **13** was recrystallized from 95% ethanol to afford orange plates: mp 100.5–101 °C (lit.[13] mp 99–100 °C, orange plates from benzene); ir 5.83 (C=O) and 6.26 μ (C=C); NMR ($CDCl_3$) δ 7.61–7.20 (m); mass spectrum *m/e* 242 (M + 2), 240 (M^+, base), 205 (–Cl), 177 (–Cl, –CO), 176, and 88.

Reaction of Thionyl Chloride with β-Phenylcinnamic Acid. A mixture of 4.48 g (0.02 mol) of β-phenylcinnamic acid,[19] 0.2 ml of pyridine, and 16.8 g (0.14 mol) of thionyl chloride was heated at reflux (bath temperature 95–100 °C) for 48 h. The infrared spectra recorded after 24 and 48 h were shown to be identical. After excess thionyl chloride was removed by distillation the residue was dissolved in 50 ml of hexanes, filtered to remove pyridine hydrochloride, and concentrated to yield 4.38 g of yellow oil, a mixture of acid chlorides. The mixture (100 mg) in 2 ml of acetone was heated with 2 ml of 2 N sodium hydroxide solution on a steam bath till acetone was evaporated and a clear aqueous solution was formed. Acidification with dilute hydrochloric acid afforded, after filtration and drying, 80 mg of a mixture of acids. Recrystallization of the mixture from benzene gave 25 mg of **8b**, mp 198–200 °C (lit.[8] mp 199–200 °C), the infrared spectrum being identical with that of **8b** previously obtained. Further crystallization of the mother liquor from ligroin afforded 50 mg of crude 2-chloro-3-phenylpropenoic acid, mp 127–136 °C (lit[13] mp 136 °C).

To a stirred solution of half (2.20 g) of the above mixture of acid chlorides in 150 ml of dry methylene chloride was added portionwise at 2–3 °C approximately 2.2 equiv (2.26 g) of aluminum chloride. The temperature of the solution (dark green) was raised and maintained at 25 °C for 30 min. The solution was decomposed with 50 ml of 6 N hydrochloric acid, the layers were separated, and the aqueous layer was extracted with methylene chloride (50 ml). The combined methylene chloride solution was successively washed with water, saturated sodium bicarbonate solution, and saturated salt solution, dried ($MgSO_4$), and evaporated to yield 1.90 g of a mixture of solids. The mixture was separated on an alumina (activity grade III, 70 g) column. Elution with 50 ml of petroleum ether–ether (10:1) gave after recrystallization from ligroin, 0.80 g (33.2%) of ketone **13**, mp 99–101 °C (lit.[13] mp 99–100 °C). Further elution with benzene (500 ml) afforded, after recrystallization from ligroin, 0.82 g (35%) of **14** as red needles, mp 194–196 °C (lit.[14] mp 195–196 °C); the infrared spectra of **13** and **14** were identical with those of authentic samples.

Benzo[*b*]thiophene 14 from Sulfenyl Chloride 11d. To 1.83 g (5 mmol) of **11d** (83% purity) in 30 ml of dry benzene was added 1.5 g (1.1 mmol) of aluminum chloride portionwise at 10 °C. The mixture was stirred at 10–15 °C for 1 h and decomposed with 6 N hydrochloric acid (50 ml), and the layers were separated. The aqueous layer was extracted with benzene (50 ml × 2). The combined benzene layers were successively washed with water and saturated sodium bicarbonate solution, dried ($MgSO_4$), and concentrated to yield 1.73 g of dark red solid. The solid was placed on a column containing 50 g of alumina (activity grade II) and eluted with petroleum ether–benzene (5:1) into seven fractions (50 ml each) and with a 1:1 mixture of the same solvent pair into ten more fractions (75–100 ml each). Recrystallization of fractions 5–9 from methanol afforded a total of 0.5 g (42%) of **14** as red needles, mp 195–196 °C. Mixture melting point with an authentic sample showed no depression, and the infrared spectrum was identical with that of an authentic sample.

Registry No.—**3b**, 103-26-4; **3d**, 830-09-1; **3e**, 619-89-6; **4a**, 21815-91-8; **4b**, 34576-87-9; **4c**, 59812-34-9; **4d**, 59812-35-0; **4e**, 59812-36-1; **6**, 59812-37-2; **7a**, 501-52-0; **7b**, 606-83-7; **7c**, 4593-90-2; **8a**, 6314-28-9; **8b**, 29491-86-9; **8c**, 41280-76-6; **8d**, 3133-81-1; **9a**, 1083-30-3; **9b**, 5195-24-4; **10a**, 59812-38-3; **10b**, 59812-39-4; **10c**, 59812-40-7; **11a**, 21815-89-4; **11c**, 39252-25-0; **11d**, 39252-24-9; **13**, 13093-22-6; **14**, 23339-77-7; thionyl chloride, 7719-09-7; methyl *p*-nitrobenzoate, 619-50-1; benzalpinacolone, 538-44-3; 2-chlorocarbonylbenzo[*b*]thiophene, 39827-11-7; 3-phenylbutanoic acid, 4593-90-2; β-phenylcinnamic acid, 606-84-8; 2-chloro-3-phenylpropenoic acid, 1727-39-5.

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Trapping of Thiaziridinimines with Imines and Nitriles

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Thermolysis of 4-benzyl-5-tosylimino-1,2,3,4-thiatriazoline (**1**) at 60–70 °C in the presence of imines and nitriles furnished respectively 5-tosylimino-1,2,4-thiadiazolidines (**4**) and 5-tosylimino-1,2,4-thiadiazolines (**5**) in good yields. Structure elucidation was based on spectral analyses and, in the case of **5**, on an independent synthesis and a crystal structure analysis. The ^{13}C NMR spectra of the new heterocycles are discussed by comparison with several model compounds.

Thiaziridinimines or their ring-opened 1,3-dipolar species (e.g., **2**) have never been isolated, but their existence during the thermal conversion of 4-alkyl-5-sulfonyl-1,2,3,4-thiatriazolines into sulfonylcarbodiimides (e.g., **1** → **3**), has recently been demonstrated.[1,2] Thus, intermediate **2** was efficiently trapped with suitable olefins, acetylenes, keto-stabi-