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Oxidations By Thionyl Chloride. Mechanism of 3-Thietanone Formation. I[1]

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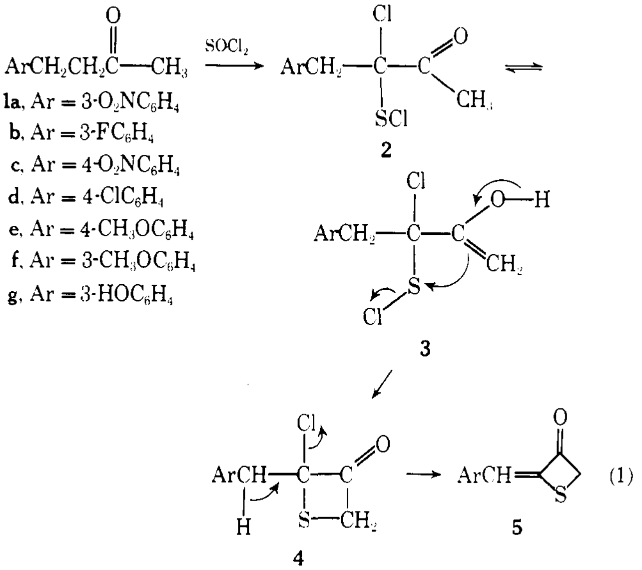
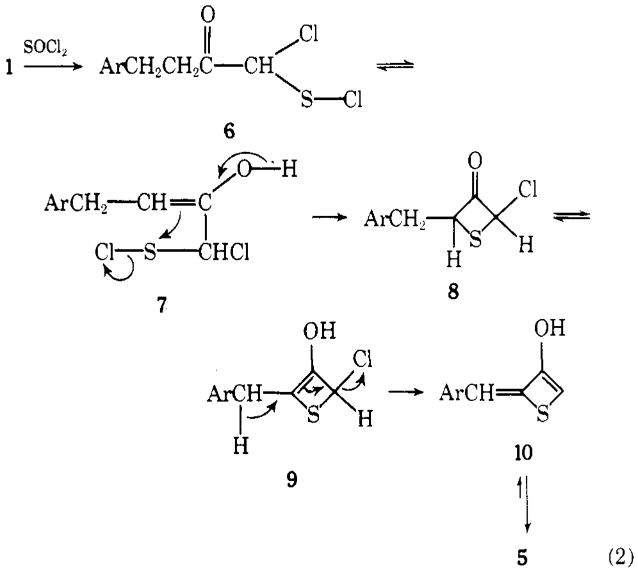
To distinguish between a mechanism in which thionyl chloride oxidizes a methylene group from one in which thionyl chlorides oxidizes a methyl group while converting monosubstituted acetones into 3-thietanones, a series of 4-aryl-2-butanones was subjected to oxidation conditions (thionyl chloride, 25–85°, 5 min–3 hr). Butanones with the following ring substitution gave only 3-thietanones as products: 3-NO_2, 3-F, 4-NO_2, 4-Cl, 4-CH_3O. However, 4-(3-hydroxyphenyl)-2-butanone gave only 2-acetyl-5-hydroxybenzo[*b*]thiophene, and 4-(3-methoxyphenyl)-2-butanone gave both 2-(3-methoxybenzylidene)-3-thietanone and 2-acetyl-5-methoxybenzo[*b*]thiophene as products. The results are consistent only with thionyl chloride oxidation proceeding exclusively at the methylene position.

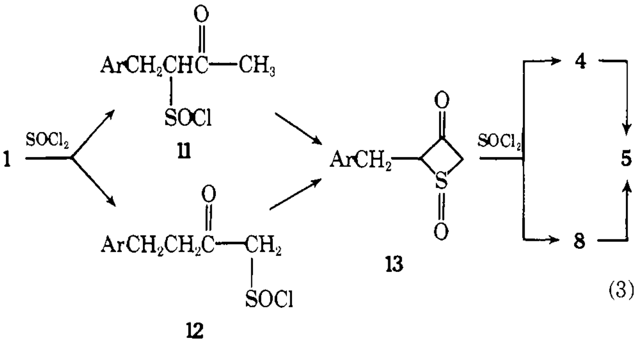
A few years ago we reported the oxidative conversion of *β*-aryl carboxylic acids and certain ketones to benzo[*b*]thiophenes[2] and of methyl ketones to 3-thietanones.[3] The unusual nature of these products and the generality of the reactions prompted us to examine the mechanism by which these products were being formed. The results of our investigation of the benzothiophene case have been reported.[2] The key to the mechanism was the intermediacy of sulfenyl chlorides by oxidation of a methylene group adjacent to the carbonyl function.

On the reasonable assumption that the 3-thietanones were being formed through the intermediacy of a structurally similar sulfenyl chloride, we proposed[3] a mechanism for 3-thietanone formation (eq 1). However, this mechanism did not seem to account for the lack of benzothiophene formation in those cases where Ar (in eq 1) is an aromatic ring. If for some reason oxidation of the methyl ketone occurred at the methyl rather than the methylene group, an alternative mechanism (eq 2) for 3-thietanone formation could be proposed that would satisfactorily explain the absence of benzothiophene formation. Disregarding, as far as this paper is concerned,[4] the implications of a third possible mechanism (eq 3) for 3-thietanone formation that seemed to combine the features of both previous mechanisms, we determined to distinguish, if at all possible, between the first two mechanisms. We herewith report our initial findings.



1a, Ar = 3-$O_2NC_6H_4$
b, Ar = 3-FC_6H_4
c, Ar = 4-$O_2NC_6H_4$
d, Ar = 4-ClC_6H_4
e, Ar = 4-$CH_3OC_6H_4$
f, Ar = 3-$CH_3OC_6H_4$
g, Ar = 3-HOC_6H_4





Results and Discussion

The techniques that we had employed quite successfully in the elucidation of the mechanism of benzothiophene formation (e.g., detection, isolation, and/or synthesis of intermediate species) were not easily available to us here, since the reaction usually proceeded readily at room temperature but not at temperatures much below that (e.g. 0°). Furthermore, the major feature of the reaction of thionyl chloride with methyl ketones was the appearance of a nicely intractable black tar from which only the 3-thietanone could be obtained.

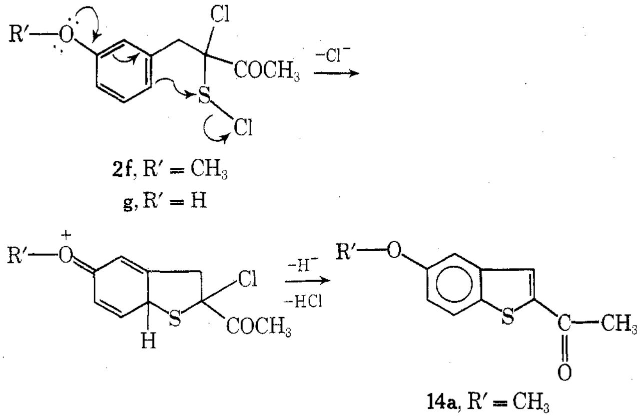
To simplify our considerations, we assumed that either **4** or **8**, but not both, was an intermediate leading to **5**. If so, then in the first two mechanisms either **2** or **6** would be formed. If **6** were the intermediate, it was not obvious how a benzothiophene could arise under any conditions. However, if **2** were the intermediate, then it should be possible to find conditions under which at least some benzothiophene could be detected, i.e., a crossover point between intramolecular cyclization to thietanone vs. benzothiophene should exist at which both products should be observed. This procedure thus would allow us to distinguish between the two mechanisms by a technique, product analysis, that *was* available to us in this case.

We previously had determined[2] that benzothiophenes form readily in a thionyl chloride reaction when (a) there is an electron-withdrawing substituent at the benzylic carbon atom (β to the carbonyl group) or (b) there is a strongly electron-donating ring substituent that can interact through resonance with the sulfur atom of the sulfenyl chloride group in a nucleophilic displacement reaction. We therefore examined the reaction mixtures of thionyl chloride with a number of variously substituted 4-phenyl-2-butanones, anticipating the appearance of benzothiophenes under condition b if **2** were the intermediate. The gross results are reported in Table I.

Table I
Products from Reaction of 4-Aryl-2-butanones with Thionyl Chloride

$XC_6H_4CH_2CH_2C$-($=$O)CH_3, when X is	Conditions	Yield, %	
		Thietanone	Benzothiophene
3-NO_2	70°, 45 min	43	
3-F	70°, 40 min	39	
4-NO_2	66°, 35 min	25	
4-Cl	85°, 3 hr	24	
4-CH_3O	85°, 2 hr	11	
3-CH_3O	51°, 12 min	2	13
3-OH	25°, 5 min		17

The data are consistent with the concerted elimination–cyclization (CEC) mechanism proposed earlier,[2e] in that benzothiophene formation occurred under conditions b stipulated above. Such participation should be strong in the case of the 3-hydroxy derivative, **2g**, and indeed no 3-thietanone is observed here. Under these conditions, then, cyclization onto the aromatic ring to form a benzothiophene competes quite favorably with cyclization onto enol **3** to form a thietanone.



2f, R′ = CH_3
g, R′ = H

14a, R′ = CH_3
b, R′ = H

Finally, the absence of thietanone formation in the case of the 3-hydroxy derivative suggests the exclusive operation of the first (eq 1) rather than the second (eq 2) mechanism. Even if the second mechanism operated simultaneously with the first, thietanone formation should be observed in every case. The absence of a 3-thietanone (which, under our work-up conditions, would have been detected even if present in less than 1% yield) in this case eliminates **6** as an intermediate. It would appear that benzothiophene formation competes most effectively with thietanone formation when the benzene ring contains strongly electron-donating substituents.

Experimental Section

Thionyl chloride (purified grade) was distilled from either triphenyl phosphite through a 30-cm Vigreux column or dipentene and then linseed oil;[5] the fraction with boiling range 75–76° was retained. Infrared spectra were obtained on Perkin-Elmer Model 457 or 257 spectrophotometers; solid samples were taken as potassium bromide pellets and liquid samples were taken as a neat film unless otherwise specified. Mass spectra were processed by Mr. Dick Weissenberger with an AEI MS-9 mass spectrometer,[6] unless otherwise noted, at 70 eV. The nuclear magnetic resonance spectra were taken on a Varian Model A-60 spectrometer, using tetramethylsilane as the internal reference and $CDCl_3$ as solvent unless otherwise specified. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. Low-boiling petroleum ether (30–60°) was used unless otherwise stated. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., and by Galbraith Laboratories, Inc., Knoxville, Tenn.

2-(3-Nitrobenzylidene)-3-thietanone (5a). To a mixture of 1.93 g (0.01 mol) of 4-(3-nitrophenyl)-2-butanone[7] (**1a**) and 0.33 ml of pyridine under dry nitrogen and in an oil bath at 70° was added over a 30-sec period 4.17 g (0.035 mol) of thionyl chloride. The mixture darkened and gas evolved after 0.5 min. At the end of 45 min excess thionyl chloride was removed in vacuo, the residue was mixed with 1:4 chloroform–benzene, and solvent was evaporated. This residue was dissolved in chloroform and mixed with 10 g of silica gel (activity III). Solvent was evaporated and the residue was placed on a silica gel column (125 g, activity III). Subsequent elution with 3 l. of 1:1 benzene–petroleum ether afforded a yellow solid which upon crystallization from carbon tetrachloride yielded 0.95 g (43%) of **5a** as yellow grains: mp 138–139.5°; ir 1528 and 1360 cm^{-1}; NMR δ 8.16–8.03 (2 H, m), 7.58–7.45 (2 H, m), 7.18 (1 H, s), and 4.43 (2 H, s); mol wt (mass spectrum) for $^{12}C_{10}{}^{1}H_7{}^{14}N^{16}O_3{}^{32}S$ 221.01479 (calcd 221.01466).

Anal. Calcd for $C_{10}H_7NO_3S$: C, 54.29; H, 3.19: N, 6.33; S, 14.49. Found: C, 54.20; H, 3.23; N, 5.97; S, 14.30.

2-(3-Fluorobenzylidene)-3-thietanone (5b). To a mixture of 1.66 g (0.01 mol) of 4-(3-fluorophenyl)-2-butanone[8] (**1b**) and 0.33 ml of pyridine under dry nitrogen was added at room temperature over a 1-min period 4.17 g (0.035 mol) of thionyl chloride. No detectable reaction occurred after 7 min. The mixture was placed in an oil bath at 70°, and after 2 min gas evolved steadily. After 40 min excess thionyl chloride was removed in vacuo, the residue was dissolved in 1:4 chloroform–benzene, and solvent was evaporated. The latter residue was dissolved in chloroform, 10 g of silica gel (activity III) was added, and solvent was evaporated. The latter residue was placed on a silica gel column (100 g, activity III). Subsequent elution with 10 l. of 1:9 benzene–petroleum ether afforded a yellow solid, which, upon sublimation (54°, 0.02 mm) and recrystallization from methanol, yielded 0.77 g (39.4%) of **5b** as light yellow needles: mp 96–97°; ir 1745 cm^{-1}; NMR δ 7.16 (4 H, cm), 7.03 (1 H, s), and 4.48 (2 H, s); mol wt (mass spectrum) for $^{12}C_{10}{}^{1}H_7{}^{19}F^{16}O^{32}S$ 194.02063 (calcd 194.02016).

Anal. Calcd for $C_{10}H_7FOS$: C, 61.84; H, 3.63; F, 9.78; S, 16.51. Found: C, 61.74; H, 3.54; F, 10.17; S, 16.80.

2-(4-Nitrobenzylidene)-3-thietanone (5c). Over a 30-sec period 4.17 g (0.035 mol) of thionyl chloride was added to a mixture of 1.93 g (0.01 mol) of 4-(4-nitrophenyl)-2-butanone[9] (**1c**) and 0.33 ml of pyridine surrounded by an oil bath at 66°. The mixture darkened and gas evolved after 3 min. At the end of 35 min excess thionyl chloride was removed in vacuo, the residue was dissolved in 1:4 chloroform–benzene, and solvent was evaporated. The latter residue was dissolved in chloroform and 10 g of silica gel (activity III) was added. Solvent was evaporated and the residue was placed on a silica gel column (100 g, activity III). Elution with 6 l. of 1:2.3 benzene–petroleum ether and 6 l. of 1:1 benzene–petroleum ether, followed by preparative TLC, furnished a yellow solid which, upon recrystallization from methanol, furnished 0.553 g (25%) of **5c** as yellow needles: mp 187–188.5°; ir 1753, 1512, and 1338 cm^{-1}; NMR (Me_2SO-d_6) δ 8.34 (2 H, A of AB quartet, J = 8.8 Hz), 7.73 (2 H, B of AB quartet, *J* = 8.8 Hz), 7.50 (1 H, s), and 4.81 (2 H, s); mass spectrum *m/e* 221 (M^+), 191 (−NO), and 175 ($-NO_2$); mol wt (mass spectrum) for $^{12}C_{10}{}^{1}H_7{}^{14}N^{16}O_3{}^{32}S$ 221.01496 (calcd 221.01466).

Anal. Calcd for $C_{10}H_7NO_3S$: C, 54.29; H, 3.19; N, 6.33; S, 14.49. Found: C, 54.39; H, 3.30; N, 6.10; S, 14.31.

Further elution of the column and preparative silica gel TLC produced a dark yellow oil subsequently identified as starting material (48% recovery).

Ethyl 3-(4-Aminophenyl)propanoate. A mixture of 20.81 g (0.094 mol) of ethyl 4-nitrocinnamate dissolved in 150 ml of warm ethyl acetate and 0.5 g of 10% palladium on charcoal was cooled in an ice bath and stirred vigorously magnetically as a total of 8.42 l. of hydrogen (low-pressure hydrogenation apparatus) was absorbed. Catalyst was removed by suction filtration through Celite, and the filtrate was dried ($CaSO_4$) and filtered. Removal of solvent afforded a crude product that was vacuum distilled to yield 17.51 g (96.5%) of ethyl 3-(4-aminophenyl)propanoate as a very pale yellow liquid: bp 127° (0.03 mm) [lit.[10] bp 121–123° (0.02 mm)]; ir 3450, 3375, and 1725 cm^{-1}.

3-(4-Aminophenyl)propanoic Acid Hydrochloride. A mixture of 17.51 g (0.091 mol) of ethyl 3-(4-aminophenyl)propanoate and 4 g (0.1 mol) of sodium hydroxide was dissolved in 50 ml of water, stirred vigorously for 1 hr, and made acidic with concentrated hydrochloric acid. Water was evaporated and the residue was treated with 150 ml of hot absolute ethanol. Insoluble sodium chloride was removed by filtration and solvent by evaporation to yield 16.57 g (91%) of 3-(4-aminophenyl)propanoic acid hydrochloride as grayish-white needles, mp 193–195° dec.

3-(4-Chlorophenyl)propanoic Acid. To a cooled (0°) solution of 16.57 g (0.083 mol) of 3-(4-aminophenyl)propanoic acid hydrochloride in 60 ml of water and 14.1 ml (0.17 mol) of concentrated hydrochloric acid was added a solution of 5.87 g (0.085 mol) of sodium nitrite dissolved in 16 ml of water; the temperature of the mixture was kept between 0 and 5° during the addition and 10 min after addition was complete. The mixture was then added rapidly to a stirred, cold solution of 9.01 g (0.091 mol) of cuprous chloride[11] dissolved in 45 ml of concentrated hydrochloric acid. The immediate formation of a yellow precipitate was accompanied by gas evolution. The mixture was stirred at room temperature for 5 hr and then was extracted with ether (3 × 100 ml). The combined ether layers were extracted with saturated sodium bicarbonate solution until gas evolution ceased, and this aqueous layer was made acidic with concentrated hydrochloric acid and extracted with ether (3 × 100 ml). The latter organic layer was dried ($CaSO_4$) and filtered. Removal of solvent furnished a yellow solid which, upon recrystallization from cyclohexane, yielded 6.84 g (44.8%) of the acid as dark yellow needles, mp 118–120° (lit.[12] mp 126°).

4-(4-Chlorophenyl)-2-butanone (1d). To a magnetically stirred solution of 6.84 g (0.037 mol) of 3-(4-chlorophenyl)propanoic acid dissolved in 125 ml of dry ether was added dropwise at a rate that maintained steady reflux an ethereal solution containing 1.76 g (46 ml, 0.08 mol) of methyllithium (Foote Mineral Co.). The mixture became milky yellow initially but cleared at the end of the addition. The mixture was then stirred for another 10 min. A saturated ammonium chloride solution was added dropwise with vigorous stirring until two clear layers separated. The organic layer was washed twice with water, dried ($CaSO_4$), and filtered. Removal of solvent and distillation afforded 6.30 g (93.3%) of **1d** as a colorless liquid: bp 71–74° (0.02 mm) [lit.[8] bp 107° (0.5 mm)]; ir 1715 cm^{-1} (lit.[8] ir 1715 cm^{-1}); mass spectrum *m/e* 182 (M^+).

2-(4-Chlorobenzylidene)-3-thietanone (5d). To a magnetically stirred mixture of 1.83 g (0.01 mol) of **1d** and 0.33 ml of pyridine in an oil bath at 85° was added over a 30-sec period 3.57 g (0.03 mol) of thionyl chloride. The mixture darkened and gas evolved. After 3 hr in the oil bath, the reaction mixture was steam distilled (215°) for 8 hr. The condensate was extracted with ether, and the combined extracts were dried ($CaSO_4$) and filtered. Solvent was removed and the residue was placed on a silica gel column (60 g, activity I). Subsequent elution with 4 l. of 1:3 benzene–petroleum ether furnished a yellow solid which, upon sublimation (73°, 0.18 mm) and recrystallization from petroleum ether, afforded 0.500 g (23.7%) of **5d** as yellow needles: mp 87–88°; ir 1743 cm^{-1}; NMR δ 7.31 (4 H, s), 7.17 (1 H, s), and 4.45 (2 H, s); mass spectrum *m/e* 210 (M^+).

Anal. Calcd for $C_{10}H_7ClOS$: C, 57.01; H, 3.35; Cl, 16.83; S, 15.22. Found: C, 57.01; H, 3.20; Cl, 17.01; S, 15.04.

Elution of the column also produced two oils. These were subsequently identified as mineral oil and starting material (4% recovery).

In a subsequent run, sublimation of the thietanone **5d** left 24.4 mg of a fluffy white powder: mp 153.5–154.6°; ir 2919 (w), 1777 (s), 1747 (m), 1489 (m), 1390 cm^{-1} (w); NMR δ 7.26 (2 H, A of AB, *J* = 8.6 Hz), 6.85 (2 H, B of AB, *J* = 8.6 Hz), 4.67 (1 H, s), 4.31 (1 H, A′ of A′B′, *J* = 15.5 Hz), 4.07 (1 H, B′ of A′B′, *J* = 15.5 Hz); mass spectrum[13] *m/e* (rel intensity) 250 and 248 (9 and 13, presumed to be an impurity), 212 (P + 2, 37), 210 (M^+, base), 175 (−Cl, 13), 166/164 ($-CH_2S$, 18/41), 149 (10), 147 (19), 138/136 ($-CH_2S$, −CO, 15/33).

4-(4-Methoxyphenyl)-2-butanone (1e). To a magnetically stirred solution of 18.59 g (0.103 mol) of 3-(4-methoxyphenyl)propanoic acid (Aldrich Chemical Co., recrystallized from cyclohexane) in 1 l. of dry ether was added at a rate to ensure steady reflux 110 ml (4.62 g, 0.21 mol) of ethereal methyllithium (Foote Mineral Co.). After the addition was complete, the mixture was stirred for 5 min and then to it was added with vigorous stirring and until there was a separation of layers a saturated solution of ammonium chloride. The ether layer was washed with saturated sodium bicarbonate solution (once) and water (twice), dried ($CaSO_4$), and filtered. Solvent was removed and the residue was distilled to furnish 16.70 g (91%) of **1e** as a colorless liquid: bp 72° (0.075 mm) [lit.[14] bp 72° (0.02 mm)]: ir 1713 cm^{-1} (lit.[14] ir 1710 cm^{-1}); mass spectrum *m/e* 178 (M^+).

2-(4-Methoxybenzylidene)-3-thietanone (5e). A mixture of 1.78 g (0.01 mol) of **1e** and 0.33 ml of pyridine under dry nitrogen and surrounded by an oil bath at 85° was treated with 4.17 g (0.035 mol) of thionyl chloride over a 30-sec period. Darkening and gas evolution occurred after 2 min. At the end of 2 hr excess thionyl chloride was removed in vacuo, the residue was dissolved in 1:4 chloroform–benzene, and solvent was evaporated. The latter residue was mixed with 10 g of silica gel (activity III) with the aid of chloroform, and this mixture was deposited on a silica gel column (125 g, activity III). Elution with 1:4 benzene–petroleum ether furnished a few milligrams of a yellow oil in the first 5 l. of eluent that was identified as a mixture of the starting ketone and the thietanone **5e**; and in the next 12 l. a yellow solid appeared that was sublimed (80°, 0.02 mm) and recrystallized from cyclohexane to afford 0.212 g (10.6%) of **5e** as clear yellow needles: mp 138–139°; ir 1744 cm^{-1}; NMR δ 7.40 (2 H, A of AB, *J* = 8.8 Hz), 7.29 (1 H, s), 6.99 (2 H, B of AB, *J* = 8.8 Hz), 5.54 (2 H, s), and 3.88 (3 H, s); mass spectrum *m/e* 206 (M^+).

Anal. Calcd for $C_{11}H_{10}O_2S$: C, 64.05; H, 4.89; S, 15.54. Found: C, 64.11; H, 4.60; S, 15.68.

3-(3-Methoxyphenyl)propanoic Acid. A mixture of 24.27 g (0.136 mol) of 3-methoxycinnamic acid (Aldrich Chemical Co.), 1.1 g of 10% palladium on charcoal, and 210 ml of 95% ethanol was hydrogenated (Paar apparatus) for 18 min, at which time 0.136 mol of hydrogen had been absorbed and further uptake ceased. Catalyst was removed by filtration through Celite and solvent by evaporation to yield 24.48 g (100%) of 3-(3-methoxyphenyl)propanoic acid as a white solid, mp 44–45° (lit.[12] mp 52°).

4-(3-Methoxyphenyl)-2-butanone (1f). To a mixture of 24.48 g (0.136 mol) of 3-(3-methoxyphenyl)propanoic acid and 1 l. of dry ether was added at a rate to maintain steady reflux 150 ml (6.16 g, 0.280 mol) of ethereal methyllithium (Foote Mineral Co.). After an additional 5 min of stirring after completion of the addition, a saturated ammonium chloride solution was added with vigorous stirring until two layers appeared. The ether layer was washed with saturated sodium bicarbonate solution (once) and with water (twice), dried ($CaSO_4$), and filtered. Removal of solvent, followed by distillation, furnished 16.28 g (67.2%) of **1f** as a colorless liquid: bp 152–153° (9 mm) [lit.[14] bp 82° (0.15 mm)]; ir 1713 cm^{-1} (lit.[14] ir 1705 cm^{-1}); mass spectrum *m/e* 178 (M^+).

Reaction of Thionyl Chloride with 4-(3-Methoxyphenyl)-2-butanone. 2-(3-Methoxybenzylidene)-3-thietanone (5f) and 2-Acetyl-5-methoxybenzo[*b*]thiophene (14a). A mixture of 1.78 g (0.01 mol) of **1f** and 0.33 ml of pyridine under dry nitrogen and surrounded by an oil bath at 51° was treated in 15 sec with 4.17 g (0.035 mol) of thionyl chloride. The mixture darkened and gas evolved after 1 min. After an additional 11 min excess thionyl chloride was removed in vacuo, and 1:4 chloroform–benzene was added and evaporated to remove residual reagent. The residue was mixed with 10 g of silica gel (activity III) with the aid of chloroform, and the resulting dry mixture was deposited on a silica gel column (100 g, activity III). Elution with 4 l. of 1:9 benzene–petroleum ether afforded a light yellow oil that solidified upon standing. Sublimation (60°, 0.30 mm) yielded 30 mg (1.5%) of **5f** as a yellow solid: mp 75–78.5°; ir 1760 cm^{-1}; NMR δ 7.48–7.15 (2 H, cm), 7.09–6.76 (3 H, cm), 4.40 (2 H, s), and 3.79 (3 H, s); mol wt (mass spectrum) for $^{12}C_{11}{}^{1}H_{10}{}^{16}O_2{}^{32}S$ 206.04044 (calcd 206.04015).

Elution with 7 l. of 1:4 benzene petroleum ether furnished a small amount of an oil which, by NMR and ir comparison, appears to be a mixture of the benzothiophene **14a** (see below), starting ketone, and an unidentified material.

Elution with 9 l. of 2:3 benzene–petroleum ether gave a yellow solid that was dissolved in acetone and treated with activated charcoal, sublimed (55°, 0.03 mm), and recrystallized from petroleum ether (bp 60–110°) to yield 0.268 g (13%) of **14a** as yellow needles: mp 95–97°; ir 1660 cm^{-1}; NMR[15,17] (acetone-d_6) δ 8.05 (1 H, br d, H_3, $J_{3,7} = 0.7$ Hz), 7.84 (1 H, tripled A of AB, H_7, $J_{6,7} = 8.9$, $J_{3,7} = 0.7$, $J_{4,7} = 0.7$ Hz), 7.46 (1 H, br d, H_4, $J_{4,6} = 2.5$ Hz), 7.18 (1 H, doubled B of AB, H_6, $J_{6,7} = 8.9$, $J_{4,6} = 2.5$ Hz), 3.87 (3 H, s), and 2.60 (3 H, s); mass spectrum *m/e* 206 (M^+), 191 ($-CH_3$), and 163 ($-COCH_3$).

Anal. Calcd for $C_{11}H_{10}O_2S$: C, 64.05; H, 4.89; S, 15.54. Found: C, 64.00; H, 4.80; S, 15.59.

4-(3-Hydroxyphenyl)-2-butanone (1g). A mixture of 18.89 g (0.098 mol) of **1a**,[7] 17.7 ml (0.19 mol) of concentrated hydrochloric acid, and 150 ml of 95% ethanol was hydrogenated at 15° in a low-pressure apparatus; 6.6 l. of hydrogen was absorbed. Catalyst was removed by suction filtration through Celite and solvent by evaporation to afford a thick red oil. The latter was dissolved in 250 ml of water and to this cold aqueous phase was added 18.50 ml (0.20 mol) of concentrated hydrochloric acid. The solution was cooled to 0° and to it was added over a 12-min period and at 0–3° a solution of 7.10 g (0.103 mol) of sodium nitrite in 60 ml of water. After an additional 15 min in the ice bath the reaction mixture was added dropwise over a 20-min period to 250 ml of boiling water. The latter mixture was cooled in ice and extracted with ether (4 × 200 ml). The ether phase was reduced to a volume of 100 ml, treated with activated charcoal, dried ($CaSO_4$), and filtered. Solvent was removed and the brown solid was distilled to afford 12.49 g of light yellow liquid, bp 132° (0.16 mm), that solidified upon standing. Recrystallization from benzene yielded 12.03 g (75%) of **1g** as a white solid: mp 85–86° (lit.[18] mp 87–88°); mass spectrum *m/e* 164 (M^+), 121 ($-COCH_3$).

2-Acetyl-5-hydroxybenzo[*b*]thiophene (14b). A magnetically stirred mixture of 1.64 g (0.01 mol) of **1g** and 0.3 ml of pyridine under dry nitrogen was treated over a 15-sec period with 4.17 g (0.035 mol) of thionyl chloride. Immediately the mixture turned yellow and gas evolved. At the end of 5 min excess thionyl chloride was removed in vacuo and the resulting black residue was treated with refluxing acetone. This mixture was filtered and to the filtrate was added 10 g of silica gel (activity III). Solvent was evaporated and the residue was placed on a silica gel column (90 g, activity III). Elution with 1:5 ethyl acetate–petroleum ether furnished 11 500-ml fractions, the third and fourth fractions of which were recrystallized twice from chloroform to afford 325 mg (16.9%) of **14b** as a yellow solid: mp 190–191° (analytical sample, mp 191–192°); ir 3338 and 1644 cm^{-1}; NMR[17,19] (acetone-d_6) δ 7.97 (1 H, d, $J_{3,7} = 0.7$ Hz), 7.75 (1 H, tripled A of AB, $J_{6,7} = 8.7$, $J_{3,7} = 0.7$ Hz), 7.37 (1 H, dm, $J_{4,6} = 2.4$, $J_{3,4} = 0.4$ Hz), 7.15 (1 H, doubled B of AB, $J_{6,7} = 8.7$, $J_{4,6} = 2.4$ Hz), 3.86 (1 H, s), and 2.61 (3 H, s); mass spectrum *m/e* 192 (M^+), 177 ($-CH_3$), and 149 ($-COCH_3$); mol wt (mass spectrum) for $^{12}C_{10}{}^{1}H_8{}^{16}O_2{}^{32}S$ 192.02470 (calcd 192.02450).

Anal. Calcd for $C_{10}H_8O_2S$: C, 62.48; H, 4.19; S, 16.68. Found: C, 62.36; H, 4.30; S, 16.69.

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Registry No.—**1a,** 3506-81-8; **1b,** 3506-77-2; **1c,** 30780-19-9; **1d,** 3506-75-0; **1e,** 104-20-1; **1f,** 29114-51-0; **1g,** 56363-73-6; **5a,** 56363-74-7; **5b,** 56363-75-8; **5c,** 56363-76-9; **5d,** 56363-77-0; **5e,** 56363-78-1; **5f,** 56363-79-2; **14a,** 56363-80-5; **14b,** 56363-81-6; thionyl chloride, 7719-09-7; 3-(4-aminophenyl)propanoic acid hydrochloride, 56363-82-7; ethyl 3-(4-aminophenyl)propanoate, 7116-44-1; 3-(4-chlorophenyl)propanoic acid, 2019-34-3; methyllithium, 917-54-4; 3-(4-methoxyphenyl)propanoic acid, 1929-29-9; 3-(3-methoxyphenyl)propanoic acid, 10516-71-9.

References and Notes

(1) Taken in part from the M.S. Thesis of W.E.S., The Ohio State University, 1971.

(2) (a) A. J. Krubsack and T. Higa, *Tetrahedron Lett.*, 5149 (1968); (b) *ibid.*, 4823 (1972); (c) *ibid.*, 125 (1973); (d) *ibid.*, 4515 (1973); (e) *J. Org. Chem.*, in press.

(3) A. J. Krubsack, T. Higa, and W. E. Slack, *J. Am. Chem. Soc.*, **92**, 5258 (1970).

(4) An examination of mechanism 3 currently is in progress and will be reported at a future date.

(5) M. Davis, H. Szkuta, and A. J. Krubsack, *Mech. React. Sulfur Compd.*, **5**, 1 (1970).

(6) We thank the National Science Foundation for a grant (GP-5202) to the chemistry department of The Ohio State University for the mass spectrometer.

(7) Prepared according to the procedure of Boatman, Harris, and Hauser,[8] except that the product was vacuum distilled to yield the ketone (80%) as a light yellow liquid, bp 136° (0.02 mm), that solidified upon standing.

(8) S. Boatman, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **30**, 3321 (1965).

(9) Prepared as reported,[8] except that the product was distilled from the black oil to gave the ketone (21.3%) as a light yellow oil, bp 141° (0.10 mm), that crystallized upon standing.

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(13) We are indebted to Mr. Louis Cazenavette II and to the Chemistry Department of the University of New Orleans for obtaining this spectrum on their Hitachi RMU-6E mass spectrometer.

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(15) In $CDCl_3$ the NMR positions were δ 7.84 (H_3), 7.73 (H_7), 7.29 (H_4), 7.14 (H_6), 3.85 (OCH_3), and 2.58 ($COCH_3$), with $J_{3,7} = 0.85$, $J_{4,6} = 2.4$, and $J_{6,7} = 8.8$ Hz. Attempts to obtain $J_{4,7}$ through spin decoupling measurements were unsuccessful, the system being too tightly coupled.[16]

(16) We are indebted to Dr. C. E. Cottrell of The Ohio State University nuclear magnetic resonance laboratory for attempting the spin-decoupling experiments at 90 and 100 MHz.

(17) For NMR spectra of substituted benzo[*b*]thiophenes, see (a) K. Takahashi, T. Kanda, and Y. Matsuki, *Bull. Chem. Soc. Jpn.*, **37**, 768 (1964); (b) K. Takahashi, T, Kanda, F. Shoji, and Y. Matsuki, *ibid.*, **38**, 508 (1965); (c) B. Caddy, M. Martin-Smith, R. K. Norris, S. T. Reid, and S. Sternhell, *Aust. J. Chem.*, **21**, 1853 (1968); (d) N. B. Chapman, D. F. Ewing, R. M. Scrowston, and R. Westwood, *J. Chem. Soc. C*, 764 (1968).

(18) M. Winter, *Helv. Chim. Acta*, **44**, 2110 (1961).

(19) In Me_2SO-d_6 the NMR positions were δ 9.64 (OH), 8.10 (H_3), 7.78 (H_7), 7.38 (H_4), 7.10 (H_6), and 2.61 (CH_3CO), with $J_{6,7} = 8.7$, $J_{4,6} = 2.3$, and $J_{3,7} = 0.8$ Hz. In neither of these cases could $J_{4,7}$ be resolved.