Reaction of Thiophene-2,3-dicarbonyl Chloride with Aluminum Chloride and Benzene

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The reaction of thiophene-2,3-dicarbonyl chloride (1) with $AlCl_3$ and benzene has been shown to yield 4,9-dihydronaphtho[2,3-*b*]thiophene-4,9-dione (**2**), 1,1-diphenyl-1*H*-thieno[2,3-*c*]furan-3-one (**3**), 2,3-dibenzoylthiophene (**4**), 3-benzoylthiophene-2-carbonyl chloride (**5**), and 3-benzoylthiophene-2-carboxylic acid (**6**) depending upon the reaction conditions. Ultraviolet spectroscopy was used to analyze the neutral product mixtures composed of **2, 3,** and **4.** A discussion of possible reaction pathways in which **5** apparently leads to the remaining products is included.

The objectives of the present work were to extend the previous investigations of the thiophene series to thiophene-2,3-dicarbonyl chloride in order to determine what products are produced and to attempt to gain an understanding of the mechanism of their formation.

The reaction of benzene with phthaloyl chloride[1,2] and various furan[2-4] and pyrrole[5] derivatives has been extensively investigated. The reaction with thiophene-3,4-dicarbonyl chloride has previously been reported[6] by this laboratory. The present work reports the extension of the thiophene series to thiophene-2,3-dicarbonyl chloride (**1**). Ultimately, as many as five products were isolated and characterized. Evidence indicates that 3-benzoylthiophene-2-carbonyl chloride (**5**), the only isolated keto acid chloride, leads to all the remaining products.

Scheme I depicts the reaction sequence used for this acylation study.

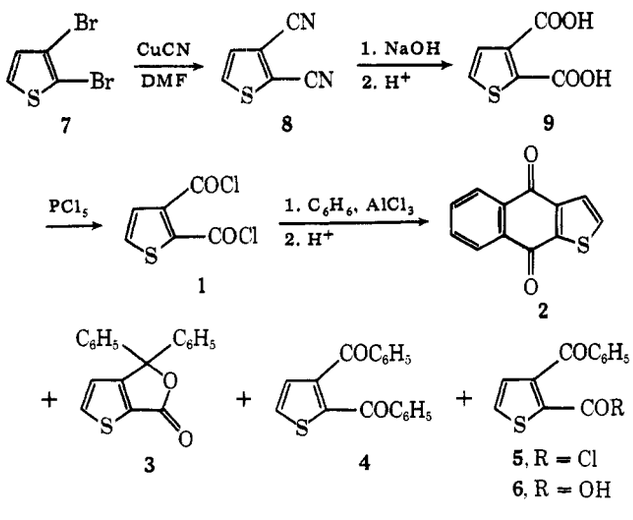
Thiophene-2,3-dicarboxylic acid (**9**) was prepared from the readily available 2,3-dibromothiophene (**7**) using a modified procedure previously used for the synthesis of thiophene-3,4-dicarboxylic acid.[7] Hydrolysis of 2,3-dicyanothiophene (**8**) using aqueous NaOH instead of the previously used ethylene glycol–KOH allowed for a more facile isolation of **9.** Substitution of phosphorus pentachloride for the previously used thionyl chloride in the synthesis of **1** eliminated the formation of thiophene-2,3-dicarboxylic acid anhydride which was shown to be present in significant amounts when thionyl chloride was used to produce **1** from **9.**

Initial investigations of product mixtures formed by the acylation of benzene with **1** readily yielded the previously described 4,9-dihydronaphtho[2,3-*b*]thiophene-4,9-dione (**2**).[7] A second neutral product, later shown to be 1,1-diphenyl-1*H*-thieno[2,3-*c*]furan-3-one (**3**), was also isolated. Residual oils of the neutral fraction indicated (TLC) a third product, later shown to be 2,3-dibenzoylthiophene (**4**). Washing the initial acylation mixtures with $NaHCO_3$ yielded a keto acid, shown to be 3-benzoylthiophene-2-carboxylic acid (**6**). Under mild reaction conditions **5** could readily be isolated as the major product.

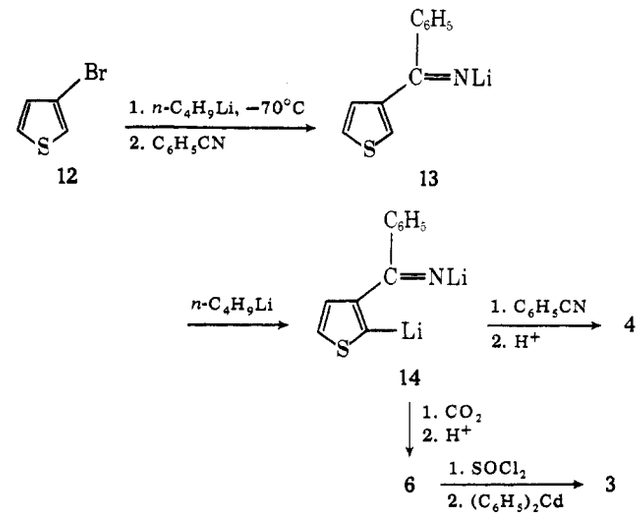
Identification of **3–6** required independent synthesis. Since **3, 5,** and **6** each have one positional isomer that theoretically could be a product, these isomers also required synthesis.

The keto acid **6**,[8] and its isomer 2-benzoylthiophene-3-carboxylic acid (**10**)[9] have been reported. The lengthy synthetic sequences described precluded their use in this work. Schemes II and III describe the routes used for the synthesis

Scheme I



Scheme II



Scheme III

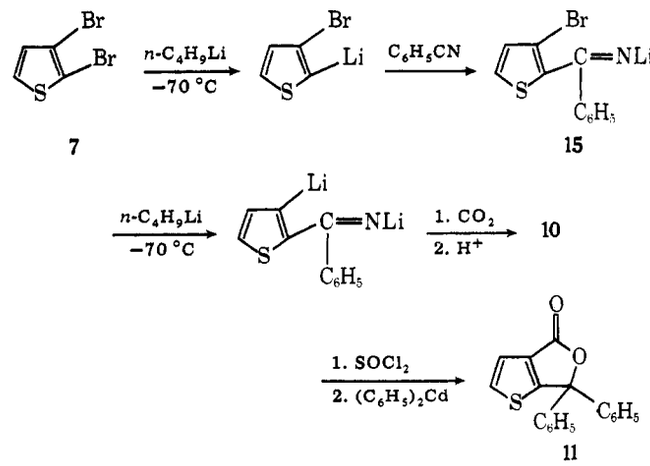


Table I. Reaction Conditions and Product Yield Data for the Acylation of Benzene with 1

Run[a,b]	Moles of C_6H_6	Solvent	Temp, °C	% yields[c] 2	3	4	5	6
1	0.5	C_6H_6	10	2.2	67	14		1.7
2	0.5	C_6H_6	25	4.0	64	13		0.97
3	0.5	C_6H_6	50	10	62	10		1.1
4	0.5	C_6H_6	80	17	50	10		1.1
5	0.02	$(CH_2Cl)_2$	0	1.5	3.4	0.9	29	9.0
6	0.02	$(CH_2Cl)_2$	25	61	7.8	2.3		
7	0.04	$(CH_2Cl)_2$	0	1.4	48	4.8	6.5	16
8	0.04	$(CH_2Cl)_2$	25	14	62	5.8		4.7

[a] 0.02 mol of diacid chloride used. [b] 0.044 mol of $AlCl_3$. [c] An average of duplicate runs.

of **3–6, 10,** and the isomer of **3,** 3,3-diphenyl-3*H*-thieno[2,3-*c*]furan-1-one (**11**).

Use of 3-bromothiophene (**12**) in the one-pot reaction technique developed by Gronowitz and Michael[10] allowed for the consecutive introduction of two functional groups into the thiophene nucleus. Treatment of the intermediate **13** with a second mole of *n*-butyllithium and benzonitrile, followed by hydrolysis, gave **4** in 52% yield. Reaction of intermediate **14** with dry ice produced **6** in 70% yield. Lactone **3** was obtained in 62% yield by the reaction of the acid chloride of **6** with diphenylcadmium.[11] An attempted synthesis of **3** by means of the reaction of 3-thienyllithium with benzophenone followed by carboxylation at C-2 and lactonization of the expected hydroxy acid failed when the initial 3-thienyllithium–benzophenone adduct precipitated from the reaction mixture, thus preventing the desired hydrogen abstraction at C-2.

The success of Scheme III depends on the known[12] selective halogen–metal interchange of the 2-bromine of **7.** The 3-bromine permits carboxylation at C-3 to produce **10** without isolation of any intermediates formed from **7.**

With authentic samples of **2–6, 10,** and **11** available, the acylation products of Scheme I were shown to be exclusively **2–6.**

In order to acquire some insight into the acylation pathway, a number of studies were carried out. A study in which the temperature and the amount of benzene were altered, resulting in product ratio changes, was first conducted. During such preliminary studies, it became apparent that an accurate method of analysis of the initial neutral acylation mixtures was needed. Isolation of each component by column chromatography was unsuccessful. Recrystallization methods, especially of the highly soluble, difficulty crystallizable **4** would result in yield data that would surely be in error. A UV method, described in the Experimental Section, readily allowed for the analysis of the initial neutral acylation mixtures containing **2–4.**

Table I lists the yields of each component formed in the acylation of benzene with **1** under various conditions. Isolated **6** from the initial $NaHCO_3$ wash is listed as a separate column. In two cases (runs 5 and 7), **5** remained in the neutral fraction after the initial $NaHCO_3$ workup and a second $NaHCO_3$ hydrolysis was used to convert the remaining **5** to **6.** The % yield of **5** was determined from **6** isolated from this second hydrolysis procedure. The remaining mixture of **2–4** was analyzed by UV.

The 1:1 ratio of **1** to benzene (runs 5 and 6) favored the formation of **2** at 25 °C (run 6). Similar results have been reported[1] for the formation of anthraquinone from phthaloyl chloride and benzene. As the temperature was decreased (run 5), the amounts of **2–4** decreased, with **5** being isolated as the major product. The formation **5** instead of its isomer reflects the tendency of **1** to form electrophilic character at the carbonyl group C-3 in its reaction with $AlCl_3$. It is interesting to note that thiophene-2,3-dicarboxylic acid anhydride was found to react with benzene and aluminum chloride in a similar manner, forming **6** exclusively.

A 1:2 ratio of **1** benzene (runs 7 and 8) indicated **3** to be the major product. These two runs are unlike results obtained with the previously reported[6] thiophene-3,4-dicarbonyl chloride which forms the corresponding quinone as the major product under these conditions. The reduction of the amounts of **5** and **6** in run 7 vs. run 8 reflects the increased probability for the reaction to go to completion.

A number of trends were noticed when benzene was used as the solvent (runs 1–4). In each case, **3** is the major product, but the amount of **3** decreases somewhat as the temperature increases, whereas the amount of **4** does not vary much. The amounts of **6** were low, indicating nearly complete reaction of **1.**

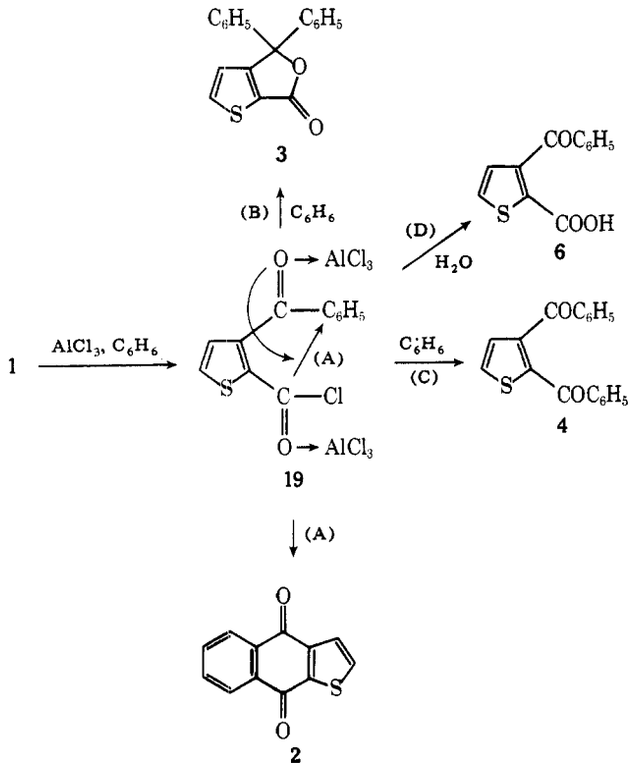
In order to acquire further mechanistic data for this reaction, experiments leading to the determination of the existence of cyclic forms of **1** were conducted. Such an intermediate could be involved in the formation of **3,** the major product in runs 1–4 and 7–8, Table I.

In the benzene series, unsymmetrical phthaloyl chloride (**16**), the pseudolactone of symmetrical phthaloyl chloride (**17**), is readily formed[13] and has been proposed[1] as the precursor to 3,3-diphenylphthalide formed in the acylation of benzene with **16.** IR analysis indicated that a carbonyl group (1790 for **17** and 1808 cm^{-1} for **16**) of any cyclic form of **1** should absorb at a higher frequency then either carbonyl of acyclic **1** (1780 and 1790 cm^{-1}). Treatment of **1** with $AlCl_3$ under conditions where **17** cyclizes to **16** resulted in recovery of acyclic **1** along with small amounts of the anhydride. Investigations of the isomeric thiophene-3,4-carbonyl chloride led to similar results. Although **3** may be formed via a low concentration of a highly reactive cyclic form of **1,** failure to isolate such species suggests its absence.

Isolation of **5** as a product in a number of acylation runs (runs 5 and 7, Table I) required investigation of its tendency to cyclize in the presence of $AlCl_3$. As in the above case of **1,** no evidence for the existence of a cyclic form of **5** could be found. Only recovery of the starting **5** contaminated with **6** was achieved. These results again contrast with the benzene series where it is known that the cyclic form of 2-benzoylbenzoyl chloride, 3-chloro-3-phenylphthalide, can be isolated and reacts with benzene in the presence of $AlCl_3$ to produce 3,3-diphenylphthalide.[14]

Although no evidence for the cyclization of **5** could be obtained, its isolation suggests its importance as an intermediate in the acylation reaction of benzene with **1.** Reaction of **5** with benzene and $AlCl_3$ at 50 °C (run 3 conditions, Table I) formed a product mixture whose composition analyzed (UV) as 2.5% **2,** 77.2% **3,** and 14.9% **4.** The acylation mixture formed with **1** at 50 °C analyzed as 8.5% **2,** 73.3% **3,** and 11.8% **4.** Since the percent composition of **2–4** usually varied by 2–3% in duplicate runs (e.g., runs 2–4, Table I) at the same conditions, the above analysis data for the acylation of benzene with **5** or **1** may be

Scheme IV



considered to be in fair agreement.

Additional evidence for the attack of the C-3 acid chloride group of **1** on benzene was achieved by the acylation of benzene with 2-benzoylthiophene-3-carbonyl chloride (**18**), the isomer of **5**. As in the reaction of **1** and **5** with benzene, **2** and **4** are produced, but also significant amounts of **11**, the isomer of **3**. Reaction of **18** at 50 °C formed a product mixture which analyzed (UV) as 28.6% **11**, 31.7% **2**, and 26.3% **4**. Since **11** was not isolated in any case when **1** was reacted with benzene, this evidence indicates the lack of importance of any intermediate formed from **1** in which the initial attack of benzene involves the C-2 acid chloride function.

In order to determine that **2–4** are final products in the acylation reaction and not precursors of one or both of the products, separate analytical samples of **2–4** were subjected to the acylation conditions at 50 °C. Each was shown to be a final product by its inertness to $AlCl_3$ in benzene.

A reaction pathway analogous to that proposed by Elderfield[15] for the acylation of benzene with phthaloyl chloride is postulated. Since no evidence could be acquired for the existence of a cyclic form of **1**, the open form is used in the proposed pathway, shown in Scheme IV. Evidence indicating that neither **2** nor **4** are formed from each other suggests a multistep pathway. Isolation of **5** and **6** as well as evidence that **2–4** and **6** can readily be formed from **5** suggests the common intermediate to be the $AlCl_3$–**5** complex shown as **19**. The four pathways ultimately leading to the isolated products are designated A, B, C, and D.

Intramolecular acylation, path A, is favored with a 1:1 ratio of **1** to benzene, provided the temperature is high enough (25 °C, run 6, Table I). The path of C-2 before reaction with a second molecule of benzene becomes important when a 1:2 ratio of **1** benzene is used (runs 7 and 8). This pathway also predominates in runs 1–4, in which benzene is used in large excess. Intermolecular acylation, path C, leading to **4** is not the major pathway in any of the acylation runs. This is perhaps due to steric hindrance by the C-3 benzoyl group of **19** to attack of the C-2 function on a second molecule of benzene. Hydrolysis of **19** (path D) leads to **6**.

Experimental Section

General. Melting points are uncorrected. All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. IR spectra were recorded on a Beckman IR-8 spectrophotometer. NMR spectra were recorded on a Varian T-60 spectrometer using approximately 10% (w/v) solutions in solvents as specified using tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. The UV spectra were determined in 95% ethanol on a Jasco ORD/UV-5 spectrophotometer. UV analysis of the neutral acylation mixtures composed of **2–4** was facilitated, since only **2** and **4** absorbed above 290 nm. Using the molar absorbtivities of **2** and **4** at 297 and 327 nm (2660 or 11 300 and 5920 or 1800) readily allowed for the determination of the concentrations of **2** and **4**. The concentrations of **3** were determined using the molar absorbtivity of **3** at 260 nm (12 500). The mixture resulting from the acylation of benzene with **18** was performed in an analogous manner.

2,3-Dicyanothiophene (8). A stirred mixture of 2,3-dibromothiophene[16] (242 g, 1.00 mol), dry CuCN (260 g, 2.90 mol), and dry DMF (350 mL) was refluxed for 4 h. The resulting mixture was cooled to 100 °C and added to a solution of $FeCl_3 \cdot 6H_2O$ (1000 g), water (1300 mL), and 12 M HCl (250 mL). The mixture was heated at 60–65 °C for 20 min, while being flushed with N_2 to rid the system of HCN. The mixture was extracted with CH_2Cl_2 (eight 500-mL portions). The organic extract was divided into two equal parts and each was washed with 6 M HCl (two 500-mL portions), water (two 750-mL portions), and saturated $NaHCO_3$ (250 mL), and then dried ($MgSO_4$). After evaporation of the CH_2Cl_2, the resulting solid was sublimed at 90 °C (0.05 mm) to give 77.7 g (58%) of **8**: mp 115–122 °C; IR (KBr) 2207 cm^{-1}; NMR (acetone-d_6) δ 7.70 (d, $J_{4,5}$ = 5 Hz, C-4 H), 8.26 (d, C-5-H).

Anal. Calcd for $C_6H_2N_2S$: C, 53.17; H, 1.50; N, 20.89; S, 23.90. Found: C, 53.48; H, 1.44; N, 20.54; S, 23.67.

Thiophene-2,3-dicarboxylic Acid (9). A stirred, N_2-flushed solution of 2,3-dicyanothiophene (33.5 g, 0.25 mol), NaOH (40.0 g, 1.00 mol), and water (200 mL) was maintained at reflux until NH_3 evolution ceased (11 h). The reaction mixture was cooled to room temperature and extracted with ether. The aqueous mixture was added dropwise to cooled, rapidly stirred 12 M HCl (130 mL). The mixture was cooled for 12 h at 0 °C. The precipitated acid was collected and recrystallized in water (1000 mL) to give 28.7–35.9 g (67–83%) of **9**: mp 287–288 °C [lit.[17] mp 270 °C]; IR (KBr) 1710 cm^{-1}; NMR (Me_2SO) δ 7.43 (d, $J_{4,5}$ = 5 Hz, C-4 H), 7.86 (d, C-5 H), 13.60 (s, -COOH).

Thiophene-2,3-dicarbonyl Chloride (1). To thiophene-2,3-dicarboxylic acid (3.44 g, 0.02 mol) was added purified PCl_5 (8.75 g, 0.042 mol) and the mixture was heated at 125–130 °C for 12 h. The resulting mixture was cooled to 20 °C and the $POCl_3$ was removed by distillation (0.1 mm). The resulting **1** was used immediately.

Reaction of Thiophene-2,3-dicarbonyl Chloride with $AlCl_3$ and Benzene. (A) Initial Investigative Run. Dry benzene (50 mL, 0.5 mol) was added to **1** and the system was heated to 50 °C. Freshly sublimed $AlCl_3$ (5.87 g, 0.044 mol) was added in small portions. After 12 h the mixture was cooled to room temperature and poured into a mixture of ice (100 g) and 6 M HCl (100 mL). Additional benzene (300 mL) was added, the layers were separated, and the benzene extract was washed with water (two 50-mL portions) and saturated $NaHCO_3$ (100 mL), and dried ($MgSO_4$). TLC (silica gel), using benzene–hexane (1:1) as eluent, indicated three major components, having R_f values of 0.07, 0.17, and 0.22. Subsequent TLC analyses of authentic **4**, **3**, and **2** were shown to have identical R_f values, respectively.

Successive recrystallizations of the mixture readily yielded **2** and **3**, identical in all respects to authentic samples. The remaining mixture was purified of **3** by refluxing (1.75 h) the mixture in 1:1 ethanol–water (15 mL) containing 1.5 g of NaOH. The resulting mixture was extracted with benzene. The benzene layer was washed with water and dried ($MgSO_3$). Evaporation of the benzene yielded an oil, which yielded **4** when crystallized from benzene–hexane (1:1). Acidification of the initial $NaHCO_3$ wash yielded the keto acid **6**, which was identical in all respects to authentic **6** prepared by Scheme I.

(B) Benzene as Solvent (runs 1–4, Table I). After a 12-h reaction time the mixture was worked up as above to yield a neutral and an acidic residue. UV analysis of the neutral residue was used to calculate the yield data of **2**, **3**, and **4**.

(C) 1,2-Dichloroethane as Solvent (runs 5–8, Table I). Dry 1,2-dichloroethane (48.2 or 46.5 mL) was added to **1** along with the appropriate volume of dry benzene (1.8 mL, 0.02 mol or 3.5 mL, 0.04 mol). After a reaction time and workup as above, the neutral fractions of runs **6** and **8** were analyzed by UV. The initial neutral fractions of runs **5** and **7** contained substantial amounts of **5** and were rehydrol-

yzed in benzene (50 mL) and saturated $NaHCO_3$. After the mixture had been refluxed (4 h) it was cooled, the layers were separated, and the benzene layer was dried and evaporated. The resulting residue was then analyzed by UV. The yield of **6** formed by the second hydrolysis procedure is listed as percent yield of **5** in Table I.

3-Benzoylthiophene-2-carboxylic Acid (6). To a stirred solution of standardized ethereal 0.812 M *n*-butyllithium (123 mL, 0.10 mol) cooled to −70 °C was added (6 min) a solution of 3-bromothiophene[18] (16.3 g, 0.10 mol) dissolved in dry ether (50 mL). After the mixture was stirred for an additional 15 min at −70 °C, a solution of benzonitrile (10.3 g, 0.10 mol) in dry ether (50 mL) was rapidly added (1 min). After the mixture was stirred for an additional 1 h at −70 °C, the mixture was allowed to warm to room temperature over a 1-h period. The mixture was heated at reflux (10 min) and cooled to 10 °C, and a second aliquot of 0.812 M *n*-butyllithium (135 mL, 0.11 mol) was added in one portion. The mixture was heated at reflux for 2 h, cooled to −70 °C, and slowly poured under N_2 into a 1-L flask half filled with crushed dry ice. The mixture was warmed to room temperature overnight and then poured into 12 M HCl and ice. The aqueous layer was extracted with ether (two 300-mL portions). The ether extract was extracted with 1 M Na_2CO_3 (400 mL), additional water was added, and the aqueous layer was acidified with 12 M HCl (150 mL). The mixture was extracted with ether (two 250-mL portions), and the ether extract was washed with water and saturated NaCl, and dried ($MgSO_4$). Evaporation of the ether and recrystallization of the residue from benzene–benzene (2:1) afforded 16.3 g (70%) of **6**: mp 154–155 °C [lit.[8] mp 148 °C]; IR (KBr) 1675 and 1715 cm^{-1}, UV_{max} (95% C_2H_5OH) 250 nm (ϵ 16 800); NMR ($CDCl_3$) δ 7.22 (d, $J_{4,5}$ = 5 Hz, C-4 H), 7.36–7.93 (m, C-5 H and Ph), 12.58 (s, -COOH).

2,3-Dibenzoylthiophene (4). To a stirred solution of standardized etheral 0.812 *n*-butyllithium (123 mL, 0.10 mol) cooled to −70 °C was added (8 min) a solution of 3-bromothiophene[18] (16.3 g, 0.10 mol) dissolved in dry ether (50 mL). After the mixture was stirred for an additional 15 min at −70 °C, a solution of benzonitrile (10.3 g, 0.10 mol) in dry ether (50 mL) was added (5 min). Stirring was continued for 1 h at −70 °C and the mixture was allowed to warm at room temperature over a 1-h period. The mixture was heated at reflux (15 min), cooled to 5 °C and 0.812 M *n*-butyllithium (123 mL, 0.10 mol) was rapidly added. The mixture was heated at reflux (2 h) and cooled to 7 °C, and a solution of benzonitrile (10.3 g, 0.10 mol) in ether (50 mL) was added (6 min). The mixture was allowed to warm (1 h) to room temperature and then poured into 1 M HCl (400 mL) and ice (200 g). The ether was removed by evaporation, then ethanol (100 mL) and 2 M HCl (50 mL) were added, and the mixture was heated at reflux (1 h). After evaporating most of the ethanol, the mixture was extracted with ether. The extract was washed with water, $NaHCO_3$ solution, and saturated NaCl solution, and dried ($MgSO_4$). Evaporation of the ether left an oil. After chromatography on neutral alumina (4.5 × 28 cm) with benzene and evaporation of most of the benzene with addition of hexane, the yield was 13.7 g (47%) of **4**: mp 80–81 °C; IR (KBr) 1640 and 1655 cm^{-1}; UV_{max} (95% C_2H_5OH) 260 nm (ϵ 16 900); NMR (acetone-d_6) δ 7.13–7.83 (m, C-4 H and Ph), 7.98 (d, $J_{4,5}$ = 5 Hz, C-5 H). Anal. Calcd for $C_{18}H_{12}O_2S$: C, 73.95; H, 4.14; S, 10.97. Found: C, 74.10; H, 4.20; S, 10.71.

2-Benzoylthiophene-3-carboxylic Acid (10). To a stirred solution of 0.749 M *n*-butyllithium (134 mL, 0.10 mol) cooled to −70 °C was added (5 min) a solution of 2,3-dibromothiophene[16] (24.19 g, 0.10 mol) dissolved in dry ether (50 mL). After the mixture was stirred (15 min) at −70 °C, a solution of benzonitrile (10.3 g, 0.10 mol) in ether (50 mL) was added (3 min). After stirring the mixture (15 min) at −70 °C, it was allowed to warm to room temperature (1.5 h). The mixture was then cooled to −70 °C and a second aliquot of 0.749 M *n*-butyllithium (150 mL, 0.11 mol) was added (5 min). The mixture was stirred (0.5 h) at −70 °C and then slowly poured onto crushed dry ice (500 g). The mixture was allowed to warm to 10 °C overnight and then poured into a mixture of 12 M HCl and ice. The mixture was heated at reflux (0.5 h), cooled, and then extracted with ether. The ether extract was then extracted with 1 M Na_2CO_3 (400 mL). The aqueous extract was acidified with 12 M HCl and extracted with ether (four 200-mL portions). The ether extract was washed with water and saturated NaCl solution, and then dried ($MgSO_4$). Evaporation of the ether and recrystallization of the remaining residue in 1:1 benzene–hexane (450 mL) afforded 13.36 g (58%) of **10**: mp 121–122 °C [lit.[9] mp 104 °C]; IR (KBr) 1655 cm^{-1}; UV_{max} (95% C_2H_5OH) 225 nm (ϵ 11 600), 280 (ϵ 7800); NMR ($CDCl_3$) δ 7.25–7.97 (m, C-4, C-5 H and Ph),12.74 (s, -COOH).

3-Benzoylthiophene-2-carbonyl Chloride (5). To 3-benzoylthiophene-2-carboxylic acid (4.65 g, 0.02 mol) was added purified $SOCl_2$ (20 mL). The mixture was heated at reflux (1 h), cooled to 50 °C, and most of the excess $SOCl_2$ was evaporated. The remaining **5** dried (25 °C) in vacuo (1 h): IR 1670, 1740 cm^{-1}; NMR δ 7.06 (d, $J_{4,5}$ = 5 Hz, C-4 H), 7.17–7.67 (m, Ph), 7.73 (d, C-5-H).

1,1-Diphenyl-1*H*-thieno[2,3-*c*]furan-3-one (3). To an etheral solution of diphenylcadmium[11] prepared from bromobenzene (4.379 g, 0.028 mol), magnesium (0.681 g, 0.028 mol), and $CdCl_2$ (2.786 g, 0.0152 mol) was added dry benzene (150 mL). The mixture was distilled to remove most of the ether. The mixture was cooled to 5 °C and a solution of **5** in dry benzene (50 mL) was added (7 min). The mixture was heated (2 h) at reflux, cooled to room temperature, and poured onto ice and 6 M HCl (100 mL). The mixture was warmed to 25 °C, the resulting liquid layers were separated, and the aqueous layer was extracted with benzene. The organic layers were combined, washed with water and $NaHCO_3$, and dried ($MgSO_4$). The benzene was evaporated, and the crude **3** was recrystallized from 1:2 benzene–hexane (100 mL) to yield 3.63 g (62%) of **3**: mp 144–46 °C; IR (KBr) 1755 cm^{-1}; NMR (acetone-d_6) δ 7.40 (s, Ph), 7.53 (d, $J_{5,6}$ = 5 Hz, C-5 H), 8.30 (d, C-5 H).

3,3-Diphenyl-3*H*-thieno[2,3-*c*]furan-1-one (11). A solution of diphenylcadmium prepared from magnesium (1.02 g, 0.042 mol), bromobenzene (6.60 g, 0.042 mol), and $CdCl_2$ (4.18 g, 0.0228 mol) was cooled to 5 °C and 2-benzoylthiophene-3-carbonyl chloride, prepared as **5**, was added (15 min). After a reaction time of 2.25 h, the mixture was worked up as in the preparation of **3** to yield 5.48 g (62%) of **11**: mp 118–119 °C; IR (KBr) 1755 cm^{-1}; UV_{max} (95% C_2H_5OH) 233 (ϵ 8300), 251 nm (ϵ 3800); NMR (acetone-d_6) δ 7.27 (d, $J_{5,6}$ = 5 Hz, C-6 H), 7.43 (s, Ph), 7.82 (d, C-5 H). Anal. Calcd for $C_{18}H_{12}O_2S$: C, 73.95; H, 4.14; S, 10.97. Found: C, 74.12; H, 4.33; S, 11.18.

Reaction of 2-Benzoylthiophene-3-carbonyl Chloride with $AlCl_3$ and Benzene. Reaction of 2-benzoylthiophene-3-carbonyl chloride with benzene and $AlCl_3$ at 50 °C afforded a neutral reaction fraction which UV analysis indicated had a composition of 26.3% **4**, 28.6% **11**, and 31.7% **2**.

Registry No.—**1**, 63599-98-4; **3**, 63609-69-8; **4**, 63599-99-5; **5**, 63600-00-0; **6**, 30006-03-2; **7**, 3140-93-0; **8**, 18853-42-4; **9**, 1451-95-2; **10**, 30011-75-7; **11**, 63600-01-1; **12**, 872-31-1; **18**, 63600-02-2; $AlCl_3$, 7446-70-0; benzene, 71-43-2; benzonitrile, 100-47-0; diphenylcadmium, 2674-04-6.

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