mmol) of 2-methylaziridine (**3d**) using the procedure given for **15**. Distillation at reduced pressure gave 0.316 g (24.2% yield): bp 59° (18 mm) [lit.[3b] bp 55° (13 mm)]; ir (CH_2Cl_2) 3350 (br), 2915 (m), 1458 (m), 1379 (m), 1364 (m), 1125 (s), 802 cm^{-1} (s).

Registry No.—**5a**, 35740-21-7; **5a** oxalate, 35740-22-8; **13**, 35740-69-3; **13** picrate, 35740-70-6; **14**, 35740-71-7; **14** picrate, 35740-72-8; **15**, 35740-73-9; **16**, 35740-23-9.

Acknowledgments.—We wish to thank the National Science Foundation (NSF Grant GY-6070) and the Rutgers Research Council for financial support.

The Reaction of Thiophene-3,4-dicarbonyl Chloride with Aluminum Chloride and Benzene

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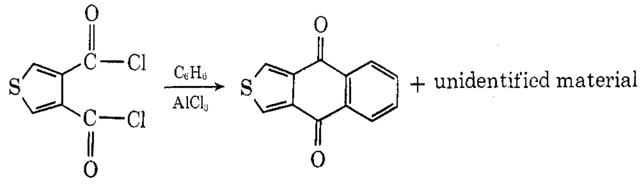
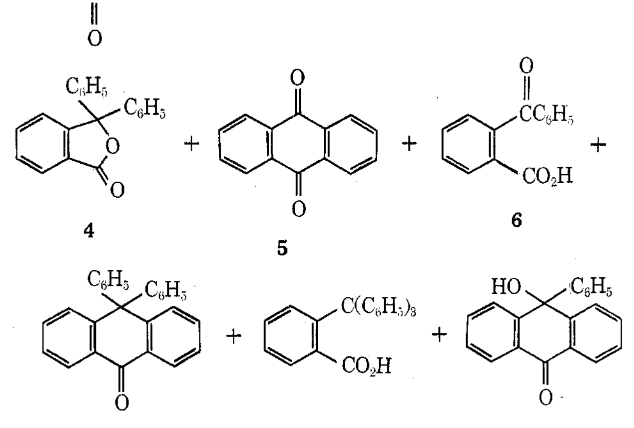
The reaction of thiophene-3,4-dicarbonyl chloride (1) with aluminum chloride and benzene has been shown to afford 4,9-dihydronaphtho[2,3-*c*]thiophene-4,9-dione (2), 1,1-diphenyl-1*H*,3*H*-thieno[3,4-*c*]furan-3-one (14), 3,4-dibenzoylthiophene (15), and 4-benzoylthiophene-3-carboxylic acid (16), depending upon the reaction conditions. These results contrast with literature reports of analogous reactions involving furan and pyrrole derivatives (10 and 11). A further example of a lactone derivative similar to 14 is seen in the treatment of 4-(α-hydroxybenzyl)-3-thiophenecarboxylic acid (26) with phosphorus pentachloride to give 1-phenyl-1*H*,3*H*-thieno[3,4-*c*]furan-3-one (28).

In an earlier report[1] concerning the synthesis of 4,9-dihydronaphtho[2,3-*c*]thiophene-4,9-dione (**2**), *via* the reaction of thiophene-3,4-dicarbonyl chloride (**1**) with benzene and aluminum chloride, there was also isolated a second reaction product whose structure was not determined at that time.



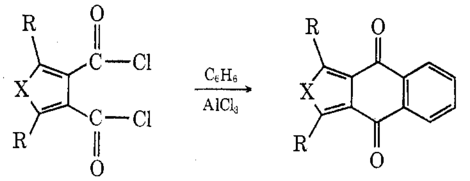
1　**2**

The reaction of phthaloyl chloride (**3**) with benzene and aluminum chloride has been studied by several workers and shown to lead to the formation of as many as six different products, **4–9**,[2] depending upon the reaction conditions.



4　**5**　**6**　**7**　**8**　**9**

There are a few reports in the literature concerning the acylation reactions of the heterocyclic analogs of phthaloyl chloride.[3] Nightingale and coworkers have studied the acylation reactions of the pyrrole derivative **10**[3b] and the analogous furan derivatives **11** with benzene.[3a,c] The only products isolated in each case were cyclic diketones **12** and **13**.



10, $R = CH_3$; $X = n\text{-}C_4H_9N$　**12**, $R = CH_3$; $X = n\text{-}C_4H_9N$
11, $R = CH_3$, C_6H_5; $X = O$　**13**, $R = CH_3$, C_6H_5; $X = O$

Attempts to acylate toluene with pyridine-2,3- and -3,4-dicarbonyl chlorides resulted in the formation of dark, intractable oils.[3c]

The unexpected isolation of a second product from the reaction of **1** with benzene and aluminum chloride motivated further study of this reaction. An investigation of this reaction involving the variation of quantities of reactants and reaction conditions was undertaken.

This study led not only to the isolation of **2**, but also to the isolation and characterization of 1,1-diphenyl-1*H*,3*H*-thieno[3,4-*c*]furan-3-one (**14**), 3,4-dibenzoylthiophene (**15**), and 4-benzoylthiophene-3-carboxylic acid (**16**). This appears to be the first report of the isolation of a heterocyclic analog of 3,3-diphenylphthalide (**4**) in an acylation reaction. The results of this investigation are summarized in Table I.

The 1:1 ratio of dicarbonyl chloride **1** to benzene (runs 1–3) appeared to favor the exclusive formation of the cyclic diketone **2**. Similar observations[2] had

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[1] D. W. H. MacDowell and J. C. Wisowaty, *J. Org. Chem.*, **37**, 1712 (1972).

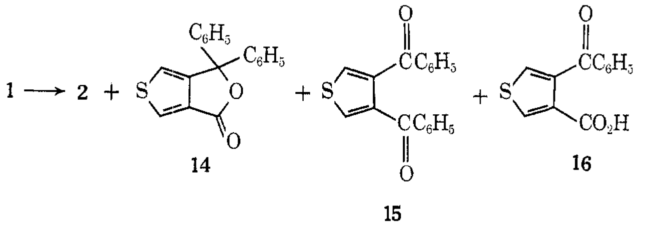
[2] M. Copisarow, *J. Chem. Soc.*, **111**, 10 (1917).

[3] (a) D. V. Nightingale and B. Sukornick, *J. Org. Chem.*, **24**, 497 (1959); (b) D. V. Nightingale and J. A. Gallagher, *ibid.*, **24**, 501 (1959); (c) D. V. Nightingale and H. L. Needles, *J. Heterocycl. Chem.*, **1**, 74 (1964).

Table I

Run	Moles of C_6H_6[e]	Solvent	Temp, °C	Yield,[g] % 2	14	15	16
1[a]	0.02	$(CH_2Cl)_2$	0	52.8			
2[b]	0.02	$(CH_2Cl)_2$	0–25	57.0			
3[c]	0.02	$(CH_2Cl)_2$	25	58.5	1–2		
4[c]	0.04	$(CH_2Cl)_2$	25	39.7	1–2		
5[d]	0.04	$(CH_2Cl)_2$	25	38.8	1–2	6.8	
6	0.5	C_6H_6	10	6.1	21.8	6.0	6.3
7	0.5	C_6H_6	25	4.4	26.2	10.8	8.0
8	0.5	C_6H_6	50	8.9	28.2	2.7	
9[f]	0.5	C_6H_6	50	7.7	29.8	11.0	

[a] **1** and C_6H_6 added at 0°. [b] **1** added at 0°; C_6H_6 added at 25°. [c] **1** and C_6H_6 added at 25°. [d] Same as *c*, but C_6H_6 added rapidly. [e] Dried over sodium. [f] Undried benzene was used. [g] Recrystallized material calculated on average of at least three runs.



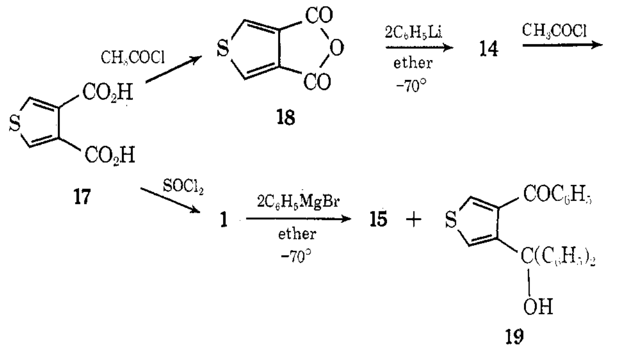
been made for the formation of anthraquinone (**5**). As the temperature was increased, the amount of **2** increased accompanied by the formation of a small amount of phthalide-type compound **14** (run 3). Higher reaction temperatures have also been shown to favor the formation of 3,3-diphenylphthalide (**4**) during the acylation of benzene with phthaloyl chloride.[2]

A 1:2 ratio of dicarbonyl chloride **1** to benzene (runs 4 and 5) showed decreased amounts of **2** and small amounts of **14** and 3,4-dibenzoylthiophene (**15**). The increased rate of addition of benzene (run 5) apparently favored the formation of **15** over **14**, possibly indicating that ring closure to a phthalide-type structure is a slower process than intermolecular acylation. This is in agreement with the observation that rapid addition of thiophene to **1** results in the formation of 3,4-bis(2-thenoyl)thiophene.[1]

Substantial changes in product distribution were observed when benzene was used as the solvent (runs 6–9). Under these conditions the yields of cyclic diketone **2** were greatly reduced (6–9%) while the yields of phthalide-type compound **14** were greatly increased (22–30%). The keto acid **16** appeared to be formed only at lower temperatures (runs 6 and 7). It has been shown that lower reaction temperatures also seem to favor the formation of *o*-benzoylbenzoic acid (**6**) during the acylation of benzene with phthaloyl chloride.[2] When undried benzene was used (run 9) in an attempt to determine the effect of traces of water on the formation of the keto acid **16**, no significant change was observed in the product distribution. The amounts of isolated diketone **15** varied slightly (3–11%) in these runs.

The formation of *o*-dibenzoylbenzene in the phthaloyl chloride acylation of benzene has not been reported.[4] Nightingale and coworkers[3a,b] did not report the formation of either the 3,4-dibenzoylpyrrole or the 3,4-dibenzoylfurans in the acylation of benzene with the corresponding dicarbonyl chlorides **10** and **11**. However, earlier work[1] has demonstrated the formation of 3,4-bis(2-thenoyl)thiophene in the acylation of thiophene with thiophene-3,4-dicarbonyl chloride (**1**). Thus, it appears at this time that the formation of the diaroyl ketones in this type of acylation reaction is unique for the thiophene nucleus.

Scheme I



The identities of 1,1-diphenyl-1*H*,3*H*-thieno[3,4-*c*]furan-3-one (**14**) and 3,4-dibenzoylthiophene (**15**) were determined by spectroscopic methods as well as by independent synthesis. The preparation of **14** by the method of Nightingale[3a] and **15** by the method of Jensen[5] are shown in Scheme I. Thiophene-3,4-dicarboxylic acid (**17**) was the starting compound in the syntheses of both **14** and **15**. Treatment of **17** with acetyl chloride[6] gave thiophene-3,4-dicarboxylic acid anhydride (**18**) in 73% yield. Addition of 2 equiv of phenyllithium at −70° to **18** afforded a sample of **14** in 6% yield, identical in all respects with **14** previously obtained from the acylation reaction. Addition of 2 equiv of phenylmagnesium bromide to **1** gave the expected diketone **15** in 17% yield. This product was also identical in all respects with the sample of 3,4-dibenzoylthiophene (**15**) obtained during the acylation reaction. A small amount (5%) of another white, crystalline solid was also isolated from the latter reaction. Spectral and analytical data are consistent with the assigned structure for α,α-diphenyl-4-benzoyl-3-thiophenemethanol (**19**).

Several different reaction pathways can be proposed for the acylation of benzene with thiophene-3,4-dicarbonyl chloride (**1**) analogous to those proposed by Elderfield[7] for the acylation of benzene with phthaloyl chloride (**3**). The different possible pathways are summarized in Scheme II. The four pathways are designated A, B, C, and D.

Intramolecular acylation, path A, is favored when there is a 1:1 ratio of **1** to benzene. When a twofold excess of benzene is used, paths B and C become important, but path A still predominates. Finally, when a large excess of benzene is used, path A becomes less important, as would be expected on statistical grounds, and path B appears to be most favorable. However, intermolecular acylation, path C, does not appear to be as favored as might be expected. This lower percentage of intermolecular acylation product may be due to steric interaction of the adjacent benzoyl groups. Path D appears to become important at lower reaction temperatures.

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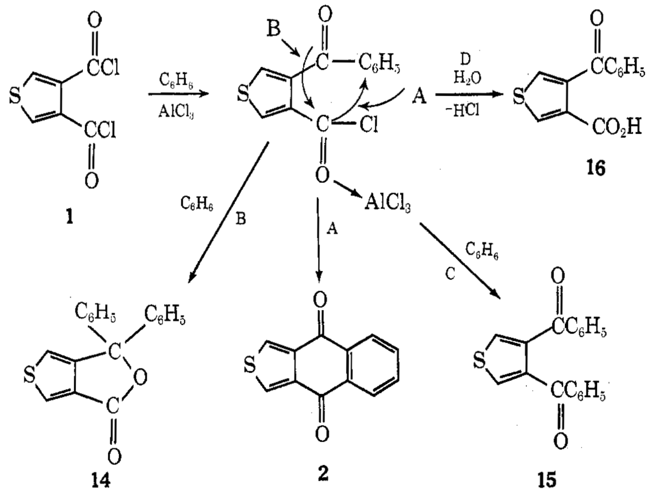
(4) A. G. Peto in "Friedel–Crafts and Related Reactions," Vol. III, Part I, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, Chapter XXXIV.

(5) F. Jensen, *J. Org. Chem.*, **25**, 269 (1960).

(6) J. Sice, *ibid.*, **19**, 70 (1954).

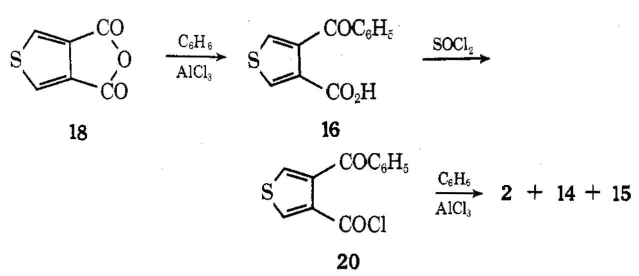
(7) R. C. Elderfield, "Heterocyclic Compounds," Vol. II, Wiley, New York, N. Y., 1951, p 101.

Scheme II

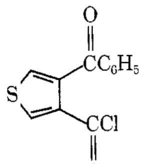


In order to determine whether 4-benzoylthiophene-3-carbonyl chloride (**20**) could act as an intermediate, **20** was synthesized and allowed to react with benzene and aluminum chloride as shown in Scheme III.

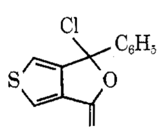
Scheme III



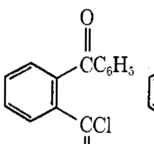
The acylation of benzene with the anhydride **18** resulted in the formation of the keto acid **16** in 63% yield.[8] The keto acid chloride **20** was formed in the usual manner and allowed to react with benzene and aluminum chloride.[9] Three reaction products were isolated: 1,1-diphenyl-1*H*,3*H*-thieno[3,4-*c*]furan-3-one (**14**), 3,4-dibenzoylthiophene (**15**), and 4,9-dihydronaphtho[2,3-*c*]thiophene-4,9-dione (**2**) in 30, 16, and 6% yields, respectively. The ir spectrum of crude **20** exhibits the distinct carbonyl frequencies at 1650 (ketone C=O) and 1750 cm^{-1} (acid chloride C=O), consistent with the normal keto acid chloride structure **20**. However, the possibility of the existence of a mixture of normal **20** and pseudo keto acid chloride **21** cannot be excluded, since the acid chloride carbonyl absorption occurs in the region of the lactone carbonyl absorption, 1760 cm^{-1}. In the case of *o*-benzoylbenzoyl chloride (**22**), it has been shown that both the normal and pseudo[10] isomer, **22** and **23**, respectively, exist, and that *both* **22** and **23** produce 3,3-diphenylphthalide (**4**) upon reaction with benzene and aluminum chloride.[11]



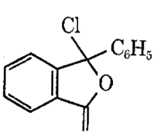
20



21



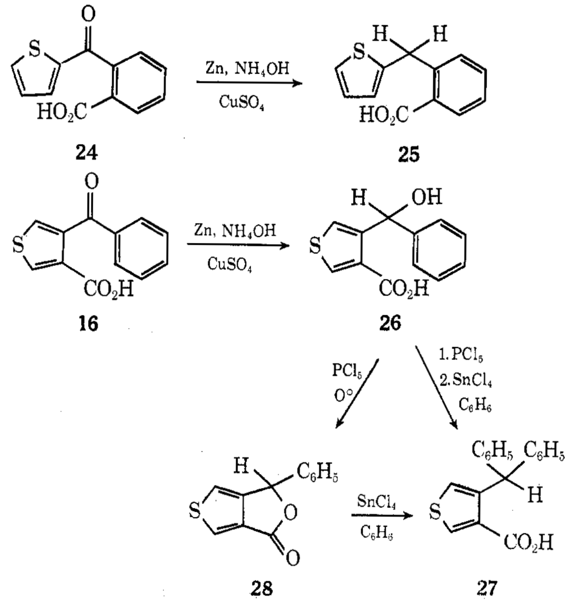
22



23

Another example of the formation of a phthalide-type derivative came to light in the course of some work paralleling the above study. Whereas reduction of *o*-(2-thenoyl)benzoic acid (**24**) with zinc and ammonium hydroxide afforded the methylene compound **25**,[12] similar reduction of the analogous 4-benzoylthiophene-3-carboxylic acid (**16**) gave the corresponding hydroxy acid **26** (Scheme IV). This acid could be converted directly to 3-benzhydrylthiophene-3-carboxylic acid (**27**) by treatment with phosphorus pentachloride followed by reaction with benzene in the presence of stannic chloride. A closer examination of this transformation showed that it proceeded *via* the lactone **28**, which could be isolated in 36% yield from the hydroxy acid **26**, by treatment at 0° with phosphorus pentachloride. The lactone **28** could be converted to the acid **27** by means of benzene and stannic chloride at 0°.

Scheme IV



Experimental Section[13]

The Reaction of Thiophene-3,4-dicarbonyl Chloride with Aluminum Chloride and Benzene.—A suspension of thiophene-3,4-dicarboxylic acid[1] (**17**) (3.44 g, 0.02 mol) in thionyl chloride (10 ml) was heated to reflux for 1 hr. The excess thionyl chloride was removed by codistillation with benzene. The resulting dicarbonyl chloride was dried *in vacuo* and used immediately.

A. 1,2-Dichloroethane as Solvent (Runs 1-5, Table I).—To a stirred suspension of aluminum chloride (5.85 g, 0.044 mol) in 1,2-dichloroethane (25 ml) was added dropwise a solution of the dicarbonyl chloride (0.02 mol) in 1,2-dichloroethane (35 ml). A solution of dry benzene (0.02–0.04 mol) in 1,2-dichloroethane was added dropwise over 15 min and the resulting brown reaction mixture was stirred for 12 hr. The dark reaction mixture was poured

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[8] P. Pirson, A. Schonne, and L. Christiaens, *Bull. Soc. Chim. Belg.*, **79**, 575 (1970).

[9] A. Haller and A. Guyot, *Bull. Soc. Chim. Fr.*, **25**, 49 (1901).

[10] H. Meyer, *Monatsh.*, **25**, 475, 1177 (1904).

[11] A. Guyot and J. Catel, *Bull. Soc. Chim. Fr.*, **35**, 1135 (1906).

[12] H. E. Schroeder and V. Weinmayr, *J. Amer. Chem. Soc.*, **74**, 4357 (1952).

[13] All temperatures are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Beckman IR-9 spectrophotometer. Nuclear magnetic resonance spectra were recorded on Varian HA-60 and Varian T-60 spectrometers using tetramethylsilane as an internal standard (τ 10) and solvents as specified.

onto ice and dilute hydrochloric acid. The organic extracts were washed with saturated sodium bicarbonate solution and water and dried ($MgSO_4$). Evaporation yielded a sticky yellow solid which was dissolved in hot benzene and placed onto a column of alumina. Elution with benzene followed by evaporation left a pale yellow solid material. This yellow solid was recrystallized from glacial acetic acid, giving pale yellow needles of 4,9-dihydronaphtho[2,3-*c*]thiophene-4,9-dione (**2**) (39–59%), mp 276–277°. The mother liquor was diluted with water and extracted with benzene. The benzene extracts were washed with saturated sodium bicarbonate solution and water and dried ($MgSO_4$). Evaporation yielded a pale yellow solid, whose ir spectrum indicated the presence of either lactone **14** and/or 3,4-dibenzoylthiophene (**15**).

The basic extract of the reaction mixture was acidified and extracted with chloroform. Evaporation yielded traces of brown crusty solid which could not be purified by chromatography over silica gel or recrystallization from the usual organic solvents.

B. **Benzene as Solvent (Runs 6–9, Table I).**—To a solution of the crude dicarbonyl chloride in dry benzene (50 ml) was added *via* Gooch tubing, in small portions, aluminum chloride (5.85 g, 0.044 mol). The resulting red suspension was stirred at room temperature for 12 hr. The reaction mixture was worked up in the manner described above. The yellow solid obtained was dissolved in hot benzene and allowed to cool slowly to give 4,9-dihydronaphtho[2,3-*c*]thiophene-4,9-dione (**2**) in 4–9% yields. The mother liquor was concentrated and the hot solution was diluted with hexane (1:1) and allowed to cool slowly; lactone **14** in 22–29% yields was obtained as a white crystalline solid, mp 156–159°. Further concentration and dilution with hexane (3:1 hexane–benzene) gave tiny white clusters of 3,4-dibenzoylthiophene (**15**) in 3–11% yields, mp 95–96°.

An analytical sample of 1,1-diphenyl-1*H*,3*H*-thieno[3,4-*c*]furan-3-one (**14**) was obtained by recrystallization from hexane–benzene (1:1): mp 159–161°; ir (KBr) 1760 cm^{-1} (lactone C═O); nmr (acetone-d_6) τ 1.76 (d, 1 H, $J_{2,5}$ = 2 Hz, thiophene), 2.12 (d, 1 H, $J_{2,5}$ = 2 Hz), 2.39–2.77 (m, 10 H, benzene).

Anal. Calcd for $C_{18}H_{12}O_2S$: C, 73.94: H, 4.13; S, 10.96. Found: C, 73.74; H, 4.10; S, 10.80.

Analytical sample of 3,4-dibenzoylthiophene (**15**) was obtained by recrystallization from hexane-benzene (3:1): mp 98–99°; ir (KBr) 1670, 1630 cm^{-1} (C═O); nmr (CS_2) τ 2.37–2.50 (m, 6 H, aromatic), 2.53–2.78 (m, 6 H, aromatic); *m/e* 292.

Anal. Calcd for $C_{18}H_{12}O_2S$: C, 73.94; H, 4.13; S, 10.96. Found: C, 74.11; H, 4.07; S, 10.99.

The basic extract was acidfied and extracted with benzene and dried ($MgSO_4$). Evaporation left 6–8% yields (runs 6 and 7) of 4-benzoylthiophene-3-carboxylic acid (**16**), mp 125–130° (lit.[8] mp 132°).

Addition of Phenyllithium to Anhydride 18.—To an ethereal solution of the anhydride **18**[6] (2.80 g, 0.018 mol) at −70° was added dropwise ethereal phenyllithium (0.036 mol) over a period of 20 min. After the addition was complete, the brick red solution was stirred at −70° for 3 hr and allowed to stir overnight at room temperature. The reaction mixture was poured into 150 ml of water, and the aqueous layer was extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and water and dried ($MgSO_4$). Evaporation gave a white, crystalline material (0.31 g, 5.8%), mp 154–156°. A mixture melting point with pure **14** obtained in the acylation experiment showed no depression.

Addition of Phenylmagnesium Bromide to Dicarbonyl Chloride 1.—Ethereal phenylmagnesium bromide prepared from bromobenzene (9.1 g, 0.058 mol) was added dropwise under nitrogen to a solution of the dicarbonyl chloride **1** (5.0 g, 0.029 mol) in ether (125 ml) maintained at −70°. The reaction mixture was poured onto ice and dilute hydrochloric acid. The ether extract was washed with saturated sodium bicarbonate solution and water and dried ($MgSO_4$). Evaporation followed by fractional crystallization (hexane–benzene) gave a white solid (0.58 g, 5.4%), mp 176–177°. The spectral and analytical data of this compound are consistent with the structure of α,α-diphenyl-4-benzoyl-3-thiophenemethanol (**19**): ir (KBr) 3300 (OH), 1625 cm^{-1} (C═O); nmr (polysol-*d*) τ 2.0–2.2 (d, 1, H, *J* = 3.0 Hz, thiophene), 3.4–3.6 (d, 1 H, *J* = 3.0 Hz, thiophene), 2.2–2.9 (m, 16 H, aromatic, alcohol).

Anal. Calcd for $C_{24}H_{18}O_2S$: C, 77.81; H, 4.90; S, 8.66. Found: C, 78.01; H, 5.03; S, 8.74.

A second crop of crystals consisted of 3,4-dibenzoylthiophene (**15**) (1.46 g, 17.3%), mp 94–96°. A mixture melting point with pure **15** obtained in acylation experiments showed no depression.

4-Benzoylthiophene-3-carbonyl Chloride (20).—A mixture of 4-benzoylthiophene-3-carboxylic acid (2.32 g, 0.01 mol) and thionyl chloride (9 ml) was stirred at room temperature overnight. The excess thionyl chloride was removed by codistillation with benzene, leaving a dark oil, ir (neat) 1650 (ketone C═O), 1750 cm^{-1} (acid chloride C═O), which was used immediately.

Reaction of 4-Benzoylthiophene-3-carbonyl Chloride (20) with Aluminum Chloride and Benzene.—The procedure for the acylation reaction and isolation of products was the same as that used in the acylation of benzene with the dicarbonyl chloride **1**.

From the acylation of dry benzene (50 ml) with **20** (2.5 g, 0.01 mol) and aluminum chloride (2.66 g, 0.02 mol) at 25° was obtained lactone **14** (0.87 g, 30%), cyclic diketone **2** (0.12 g, 5.6%), and 3,4-dibenzoylthiophene (**15**) (0.47 g, 16%). There was no evidence of keto acid **16** formation.

4-(α-Hydroxybenzyl)-3-thiophenecarboxylic Acid (26).—Into a 3-l. flask fitted with a reflux condenser and stirring bar were placed 28% ammonium hydroxide (1000 ml), copper(II) sulfate (0.5 g), 4-benzoylthiophene-3-carboxylic acid (**16**) (17.25 g, 0.074 mol), and zinc dust (50 g, 0.77 mol). The mixture was heated to reflux for 32 hr. Fresh portions (250 ml) of ammonium hydroxide were added every 3 hr.

The hot solution was then filtered and acidified with 6 *M* HCl, cooled, and extracted with ether. The ether extracts were dried ($MgSO_4$) and evaporation yielded a gummy residue which could not be recrystallized. The sodium salt of the acid was heated with Norit, filtered, and acidified to give **26** as a white solid (17.3 g, 79.8%) which was recrystallized from benzene–hexane, mp 123–124°.

An analytical sample of **26** was obtained by further recrystallization from benzene–hexane: mp 124–124.5°; ir (KBr) 3300 (OH), 3100–2500 (acid OH), 1670 cm^{-1} (C═O), nmr (acetone-d_6) τ 1.70 (d, 1 H, *J* = 3.5 Hz, thiophene), 2.40–2.80 (m, 6 H, C_6H_5 and thiophene), 3.70 (s, 1 H, methine), 4.03 (br, s, 1 H, OH).

Anal. Calcd for $C_{12}H_{10}O_3S$: C, 61.52; H, 4.30; S, 13.69. Found: C, 61.31; H, 4.29; S, 13.91.

4-Benzhydrylthiophene-3-carboxylic Acid (27).—Into a 25-ml flask were placed the hydroxy acid **26** (1.17 g, 0.005 mol) and dry benzene (15 ml). Phosphorus pentachloride (10.4 g, 0.005 mol) was added to the cooled solution in small portions. After addition was complete, the reaction mixture was heated on a steam bath for 10 min and then cooled.

To the cooled reaction mixture was added dropwise a solution of tin(IV) chloride (1.76 g, 0.8 ml, 0.007 mol) in dry benzene (15 ml). After the addition was complete, the reaction mixture was stirred at 0° for 1 hr, allowed to reach room temperature, and then heated to reflux. It was then poured onto ice and 2 *M* HCl and extracted with ether. The ether extracts were washed with sodium bicarbonate solution and water and dried ($MgSO_4$). The basic extract was acidified, extracted with ether, and dried ($MgSO_4$). The basic extract was acidified, extracted with ether, and dried ($MgSO_4$). Evaporation yielded 0.18 g of crude acid **27**. The organic extract was evaporated and 1.15 g of reddish solid was obtained. The solid was dissolved in a minimum amount of benzene and placed onto a silica gel column. Elution with benzene gave an additional 0.42 g of acid **27**, mp 170°. The total yield of acid **27** obtained was 0.60 g (41%).

Recrystallization of **27** from benzene–hexane gave a white solid: mp 170°; ir (KBr) 3150–2600 cm^{-1} (acid OH), 1680 (C═O); nmr (DMSO-d_6) τ −2.3 (br, s, 1 H, COOH), 1.80 (d, 1 H, *J* = 3.5 Hz, H_5), 2.60–3.10 (m, 10 H, C_6H_5), 3.33 (d, 1 H, *J* = 3.5 Hz, H_2), 3.80 (s, 1 H, methine).

Anal. Calcd for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79; S, 10.89. Found: C, 73.56; H, 4.79; S, 11.06.

1-Phenyl-1*H*,3*H*-thieno[3,4-*c*]furan-3-one (28).—Into a 25-ml flask were placed the hydroxy acid **26** (1.2 g, 0.005 mol) and dry benzene (10 ml). To the cooled, stirred suspension was added phosphorus pentachloride (1.0 g, 0.005 mol) in small portions. After the addition was complete, the reaction mixture was allowed to reach room temperature and then heated to reflux. The pale yellow solution was poured onto water and extracted with ether. The ether extracts were washed with saturated sodium bicarbonate solution and water and dried ($MgSO_4$). The basic extract was acidified and yielded 0.2 g of starting material. The organic layer was evaporated and the resulting oil was dissolved in benzene and placed onto a silica gel column. Elution with chloroform yielded a white solid (0.33 g, 36%), mp 98–99°.

An analytical sample of **28** was recrystallized from benzene–hexane: mp 99–100°; ir (KBr) 1760 cm^{-1} (lactone C═O);

nmr ($CDCl_3$) τ 2.05 (d, 1 H, J = 2.5 Hz, thiophene), 2.63 (s, 5 H, C_6H_5), 2.88 (q, 1 H, thiophene), 3.67 (d, 1 H, J = 1.0 Hz, methine).

Anal. Calcd for $C_{12}H_8O_2S$: C, 66.64; H, 3.73; S, 14.83. Found: C, 66.87; H, 3.55; S, 14.79.

Registry No.—**1**, 33527-26-3; **2**, 33527-20-7; **14**, 36540-46-2; **15**, 36540-47-3; **19**, 36540-48-4; **20**, 36540-49-5; **26**, 36540-50-8; **27**, 36540-51-9; **28**, 36540-52-0; aluminum chloride, 7446-70-0; benzene, 71-43-2.

1,2,4-Triazoles. XXXII. Syntheses and Correlation of Proton Magnetic Resonance Spectral Characteristics with Molecular Orbital Parameters of Derivatives of the *s*-Triazolo[4,3-*a*]quinoline and *s*-Triazolo[3,4-*a*]isoquinoline Ring Systems[1]

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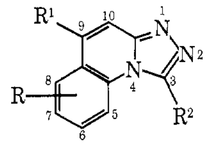
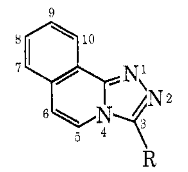
The syntheses and proton magnetic resonance (pmr) spectral data at 60 MHz for several members of the title ring systems are described. Confirmation of the spectral assignments was obtained by examination of several of the products at 100 MHz. Of particular interest are correlations observed between chemical shifts and electron densities calculated by the FEHT method. Ultraviolet absorption data for these ring systems are also described.

In a continuation of our interests in the chemistry of the *s*-triazole ring system, we have extended our study of the *s*-triazolo[4,3-*a*]pyridine and *s*-triazolo[1,5-*a*]pyridine systems[2] to include two benzo-fused derivatives, the *s*-triazolo[4,3-*a*]quinoline (**1**) and the *s*-triazolo[3,4-*a*]isoquinoline (**2**) ring systems. The influence of the fused benzene ring on the spectral and chemical properties of these ring systems is of interest as is the nature of the electron delocalization throughout these systems. The empirical correlation between chemical shifts and calculated π-electron densities in the benzenoid series[3] suggested the study of the ring systems from these viewpoints. The presence of heteroatoms in these nonalternant heterocycles requires the use of SCF[3-6] methods for the calculation of the electron densities. This method, in contrast to the simple Hückel approach, has been shown[3] to provide useful correlations of the above type. To aid in the interpretation of the pmr spectra, suitable methyl-substituted products were synthesized by the procedures described below.

Synthetic Procedures.—Reports of the synthesis of *s*-triazolo[4,3-*a*]quinoline[7] and of 9-methyl-*s*-triazolo[4,3-*a*]quinoline-3-thiol[8] appeared as early as 1900. Oxidative ring closure of various aromatic aldehyde 2-quinolyl hydrazones with ferric chloride or nitrobenzene was shown[9a] to be an effective route to 3-substituted derivatives, and the introduction of substituents into the 3 position analogous to those reported for the *s*-triazolo[4,3-*a*]pyridine system[10] was also described.[9b]



1



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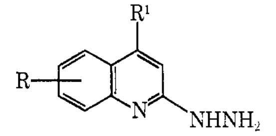

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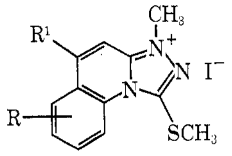

4

Standard procedures developed for other ring systems[10] were used for the synthesis of the *s*-triazolo[4,3-*a*]quinoline derivatives described in Table I. The intermediate 2-quinolylhydrazines used in the cyclization reactions were prepared in good yields from the appropriate methyl-substituted quinoline *via* the 1-methyl-2-quinolones and 2-chloroquinolines.[11] These hydrazines, with or without substituents in either the benzene or the pyridine rings, readily cyclized with aliphatic acids to the desired products except as described below. Cyanogen bromide and carbon disulfide were found to be quite effective in forming the 3-amino (**1**, R^2 = NH_2) and 3-mercapto (**1**, R^2 = SH) derivatives. 8-Methyl-2-quinolylhydrazine was found to be extremely resistant to cyclization with either formic acid or acetic acid, the *N*-formyl and *N*-acetyl

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