(7.2–7.8) (m, 10 H, ArH); mass spectrum, *m/e* 405 (M^+), 386 (M − F), 295 (M − $C_6H_5CH_2F$), 259 [$(CH_3)_2C_6H_3N(BF_2)CH_2C_6H_5$], 211 [$(CH_3)_2C_6H_3NHCH_2C_6H_5$], 210, 195 ($C_6H_5C(OBF_2)$=CHC=O), 146 ($C_6H_5COCH$=C=O), 105 ($C_6H_5CO$), 91 ($C_6H_5CH_2$).

Anal. Calcd for $C_{24}H_{22}BF_2NO_2$: C, 71.13; H, 5.47; N, 3.46. Found: C, 71.65; H, 5.50; N, 3.42.

The reaction was also conducted in ethanol solvent; substrate **4c** (3.15 g, 10 mmol) was added portionwise over 20 min to a stirred alcoholic solution of sodium ethoxide [constituted from absolute ethanol (30 mL) and sodium hydride (0.51 g of a 70% dispersion, 15 mmol)] under N_2 at 20 °C. The procedure above was continued, and **5d** was isolated in 70% yield.

***N*-Benzyl-3′,5′-dimethylbenzoylacetanilide (2d).** A mixture of **5d** (1.0 g), sodium acetate trihydrate (2 g), water (3 mL), and dimethylformamide (7 mL) was kept at ~90 °C for 0.75 h with intermittent stirring and then was poured into ice water. The product was extracted into ether, and the ethereal phase (~50 mL) was washed with water, dried (Na_2SO_4), and evaporated. The residual oil (0.8 g) was triturated with a few milliliters of aqueous methanol containing several drops of 2 M HCl and chilled when it solidified. Filtration afforded 0.62 g (71%) of **2d** (mp 89–91 °C): colorless crystals (from aqueous methanol); mp 92–93 °C; mass spectrum, *m/e* 357 (M^+), 211 [$(CH_3)_2C_6H_3NHCH_2C_6H_5$], 210, 147 ($C_6H_5COCH_2CO$), 105, 91.

Anal. Calcd for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.48; N, 3.92. Found: C, 80.68; H, 6.56; N, 3.86.

***N*-Ethyldifluoro([1-phenyl-2-(3′,5′-dimethylphenylcarbamoyl)vinyl]oxy)borane (5e).** Anilide **4c**[14] (3.15 g, 10 mmol) was alkylated with ethyl bromide (6 mL, ~70 mmol) in dimethylformamide as for **5d.** Reaction for 8 h gave **5e** (2.25 g, 66%; mp 188–190 °C): colorless tiny crystals (from aqueous ethanol); mp 189–190 °C; IR 1610 cm^{-1} (s, coordinated amide C=O); ^1H NMR ($CDCl_3$) δ 1.26 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 2.38 (s, 6 H, $ArCH_3$), 3.92 (q, *J* = 7 Hz, 2 H, CH_2CH_3), 5.42 (s, 1 H, CH), 6.84 (s, 2 H, ArH), 7.12 (s, 1 H, ArH), 7.2–7.75 (m, 5 H, ArH); mass spectrum, *m/e* 343 (M^+), 324 (M − F), 197 [$(CH_3)_2C_6H_3N(BF_2)C_2H_5$], 195 ($C_6H_5C(OBF_2)$=CHC=O), 149 [$(CH_3)_2C_6H_3NHC_2H_5$], 105 ($C_6H_5CO$).

Anal. Calcd for $C_{19}H_{20}BF_2NO_2$: C, 66.50; H, 5.88; N, 4.08. Found: C, 66.75; H, 5.78; N, 4.06.

Product **5e** was identical (IR, mixture melting point) with that derived from anilide **2e** (mp 63–64 °C) and boron trifluoride etherate (method A).[7]

In a variation of the procedure, dry tetrahydrofuran (50 mL) was added in one portion to a stirred mixture of **4c** (3.15 g, 10 mmol) and sodium hydride (0.60 g of a 70% dispersion, 17 mmol) under N_2, and stirring was continued for 30 min; the sparingly soluble **4c** dissolved with evolution of H_2, and reaction was accompanied by a fair exothermic effect. After addition of ethyl bromide (5 mL, excess) and alkylation for 8 h, **5e** was isolated in 60–65% yield.[15]

5,7-Dimethyl-*N*-ethyl-4-phenylquinolin-2-one (6). A mixture of **5e** (1.0 g) and polyphosphoric acid (10 g) was heated at 145–150 °C for 1 h with intermittent stirring and then was cooled somewhat and diluted with ice water. The product was extracted into ether (~50 mL), and the ethereal phase was washed with water, dried (Na_2SO_4), and evaporated to yield **6** as a solid [0.70 g, 88%; mp 112–114 °C; one spot on TLC (benzene)]: colorless needles (from aqueous methanol); mp 115 °C; mass spectrum, *m/e* 277 (M^+), 276 (M − 1), 262 (M − 15), 249 (M − 28), 234 (249 −15).

Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.55; H, 7.07; N, 5.15.

Action of Sulfuryl Chloride on 5e. Formation of 2,2,4′-Trichloro-3′,5′-dimethyl-*N*-ethylbenzoylacetanilide (1b). To a suspension of **5e** (0.30 g) in acetonitrile (1 mL) contained in a 25-mL conical flask was added an excess of sulfuryl chloride (1.5 mL). The flask was immediately stoppered and left to stand at room temperature for 2.5–3 h; reaction rapidly occurred with liberation of gas and dissolution of the **5e**, and the (glass) stopper was momentarily loosened now and then to alleviate the pressure in the flask. Ice water was added, and the mixture was stirred intermittently until the precipitated material had solidified. This was filtered, washed with water, and dried (0.31 g, 88%; mp 98–118 °C); IR, MS, and TLC (benzene) established the product to be **1b**[1] mixed with minor dichloroamide and negligible tetrachloroamide.[16] Chlorination for a shorter period (1–1.5 h) led to mixtures containing a decreased proportion of **1b.** Treatment of **4c** (0.30 g) in acetonitrile (1 mL) with sulfuryl chloride (1.5 mL) for 3 h, as for **1b,** afforded 2,2,2′,4′-tetrachloroanilide **1c,** associated with minor trichloro material [MS and TLC (benzene)], in almost quantitative yield. Chlorination of **5b** (0.30 g) for 2 h as for **1b** gave amide **1a** [IR, MS, TLC (benzene)] in >90% (crude) yield.

Acknowledgment. The author is grateful to the South African Council for Scientific and Industrial Research, Pretoria, for financial support and would like to thank Mr. N. Blom and Mr. A. Zafirellis for assistance with some of the experimental work and spectral determinations.

Registry No.—**1a,** 19359-43-4; **1b,** 52827-58-4; **1c,** 40624-92-8; **2d,** 68646-50-4; **2e,** 52827-50-6; **3c,** 40624-75-7; **4c** charged, 68682-89-3; **4c** uncharged, 68646-51-5; **5b** charged, 15387-97-0; **5b** uncharged, 68646-52-6; **5d** charged, 68682-90-6; **5d** uncharged, 68646-53-7; **5e** charged, 68682-91-7; **5e** uncharged, 68646-54-8; **5f** charged, 68682-92-8; **5f** uncharged, 68646-55-9; **5g** charged, 68682-93-9; **5g** uncharged, 68646-56-0; **6,** 68646-57-1; benzyl bromide, 100-39-0; ethyl bromide, 74-96-4.

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(9) Compounds **5f** (mp 113–114 °C) and **5g** (mp 136–137 °C) had IR, ^1H NMR, and mass spectroscopic and analytical data in agreement with the assigned structures.
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(11) Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Infrared spectra (KBr disk) were recorded on a Perkin-Elmer Model 521 spectrophotometer (s = strong). ^1H NMR spectra were obtained at 60 MHz using a Hitachi Perkin-Elmer R-20 instrument, with Me_4Si as an internal reference. Mass spectra (70 eV) were measured on a Varian CH-5 spectrometer. Reagent grade dimethylformamide was dried over 4Å molecular sieves. Tetrahydrofuran was distilled as needed from benzophenone sodium ketyl under N_2. Sodium hydride was used as a 70% dispersion in mineral oil. Thin-layer chromatography was performed on silica gel F_{254} precoated plates (E. Merck, Darmstadt) of 0.25-mm thickness; spots were visualized with a UV lamp, and/or in an iodine chamber.
(12) No serious attempts were made to optimize yields in the alkylations.
(13) The presence in **4** (and **5**) of acid impurity generally led to acid-catalyzed partial conversiion to **3** (and **2**) during crystallization.
(14) Crude substrate (**4c,** mp 240–245 °C) was utilized in several alkylations (to **5d** and **5e**) with equal success.
(15) The N-alkylation reaction was noticeably slower in absolute ethanol than in either dimethylformamide or tetrahydrofuran.
(16) A similar chlorination (without acetonitrile) in a flask loosely stoppered with cotton wool gave as major product "A" (mp 197–199 °C; sparingly soluble in warm ethanol; $C_{19}H_{16}Cl_5NO$ by elemental and mass specral analysis). The effect, if any, of atmospheric oxygen on the reaction remains to be clarified.

Reaction of Thionyl Chloride with 3,4-Dihydro-2(1*H*)-quinolinone

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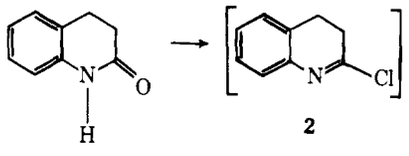
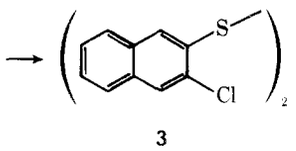
The attempted conversion of 3,4-dihydro-2(1*H*)-quinolinone, **1,** to the corresponding imidoyl chloride, **2,** using thionyl chloride in DMF gave instead of the expected imidoyl chloride a number of unusual and unexpected products. The nature



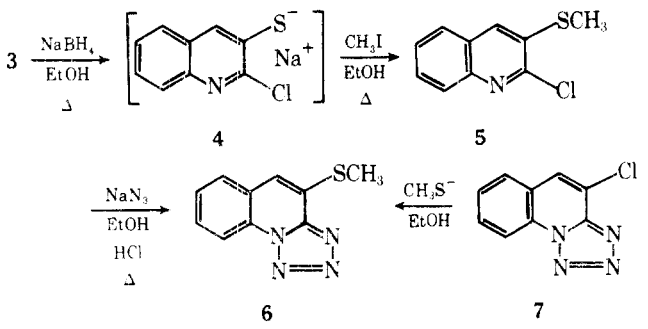
1 **2**



3

0022-3263/79/1944-0877$01.00/0

Scheme I



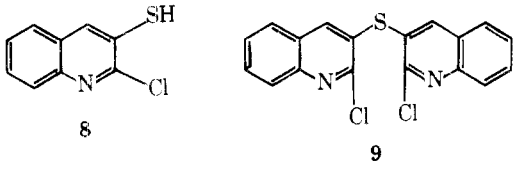
and quantity of these products depended on the reaction temperature and the order of addition of reagents.

When excess thionyl chloride was added to a DMF solution of **1** at 0–10 °C, a tan solid (**3**), mp 242 °C dec, $C_{18}H_{10}Cl_2N_2S_2$, precipitated from the reaction mixture in 40–50% yield. The NMR, mass, and IR spectra and combustion analysis suggested the disulfide structure for **3**.

The structure of **3** was confirmed chemically by its conversion to **6** by the route outlined in Scheme I.

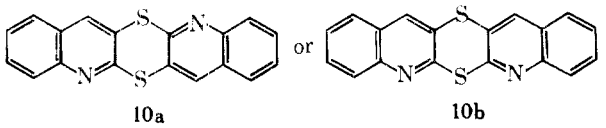
The formation of **6**, which proved to be identical with the product of the reaction of 4-chlorotetrazolo[1,5-*a*]quinoline with sodium methyl sulfide, confirmed the proposed structure for **3**.

Two additional materials, the mercaptan **8** and the sulfide **9**, both soluble in DMF, were isolated from the reaction by

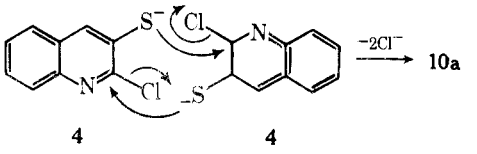


pouring the DMF filtrate into water and collecting the yellow solid that formed. The sulfide, the major constituent, could be isolated and purified by fractional crystallization to yield a white solid, mp 198–200 °C, $C_{18}H_{10}Cl_2N_2S$; its structure was determined by physical methods. The mercaptan **8** proved to be unstable and, while enough was isolated by LC for a tentative structure assignment based on spectrographic analysis, an unequivocal proof of structure was provided by its conversion to **5** by methylation.

When the reaction was carried out at higher temperature (>80 °C) or the reaction was allowed to exotherm to >80 °C, **3** still precipitated from the reaction, but in lower quantities. Two new materials were isolated from the DMF filtrate, both having identical mass spectra, NMR, and combustion analyses but differing in melting point, IR, and R_f on TLC. The pentacyclic structures **10a** and **10b** satisfied all of the physical and

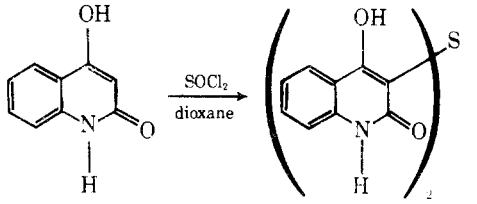


spectral data, but no simple way could be found to differentiate between them. Baranowska and Karminski[1] claim to have differentiated between two similar pentacyclic materials, **11a** and **11b**, by spectral methods, but they offered no explanation. However, we were able to differentiate between **10a** and **10b** by an alternative synthesis of **10a**. The reaction of **3** with sodium borohydride in refluxing butanol leads to a pentacyclic material identical with **10a**. It is proposed that the reaction goes through the intermediate **4**, which then dimerizes to form **10a**.



We have examined the reaction in an attempt to optimize the yields for each of the products and have observed the following: (1) a threefold excess of thionyl chloride is necessary for complete utilization of **1**; (2) the formation of **3** is optimized when DMF is added very slowly to a solution of **1** in thionyl chloride; (3) the formation of **9** is optimized when thionyl chloride is very slowly added to a solution of **1** in DMF; and (4) DMF is not necessary for the formation of **3**, **8**, and **9**. The same products result when **1** is refluxed in thionyl chloride or thionyl chloride/dioxane. We have not been able to optimize the formation of either **10a** or **10b** by changing reaction conditions.

Mechanism. Although oxidation mechanisms with thionyl chloride are well documented[2] and a number of mechanisms have been proposed for the oxidations involving thionyl chlorides and carboxylic acids and ketones,[3,4] very little has been reported on reactions between thionyl chloride and lactams. Ziegler and Kappe[5] described the reaction of 4-hydroxy-2(1*H*)-quinolinone, **12**, with thionyl chloride at high temperatures to form the quinoline sulfide, **13**. No mechanism was postulated for this reaction.

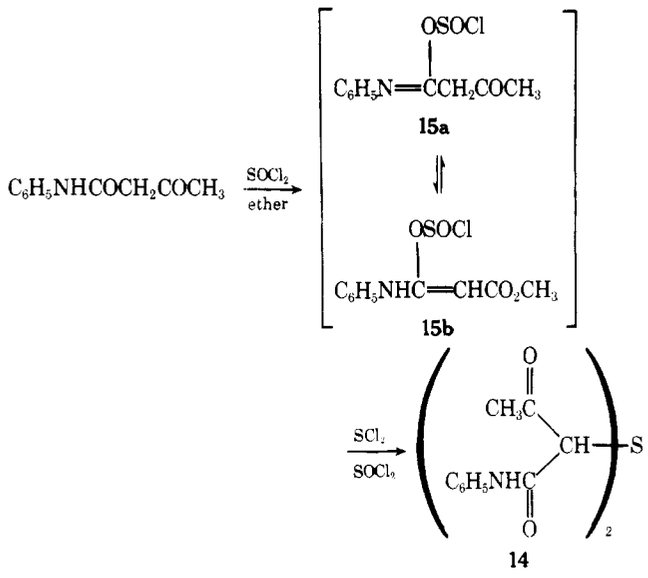


Recently, however, Oka and Hara[6] reported that the reaction of acetoacetanilide with thionyl chloride in ether led to sulfide **14**, for which they proposed a mechanism involving the attack of sulfur dichloride, a contaminant of commercial thionyl chloride, on the vinyl chlorosulfite intermediate **15b** (Scheme II).

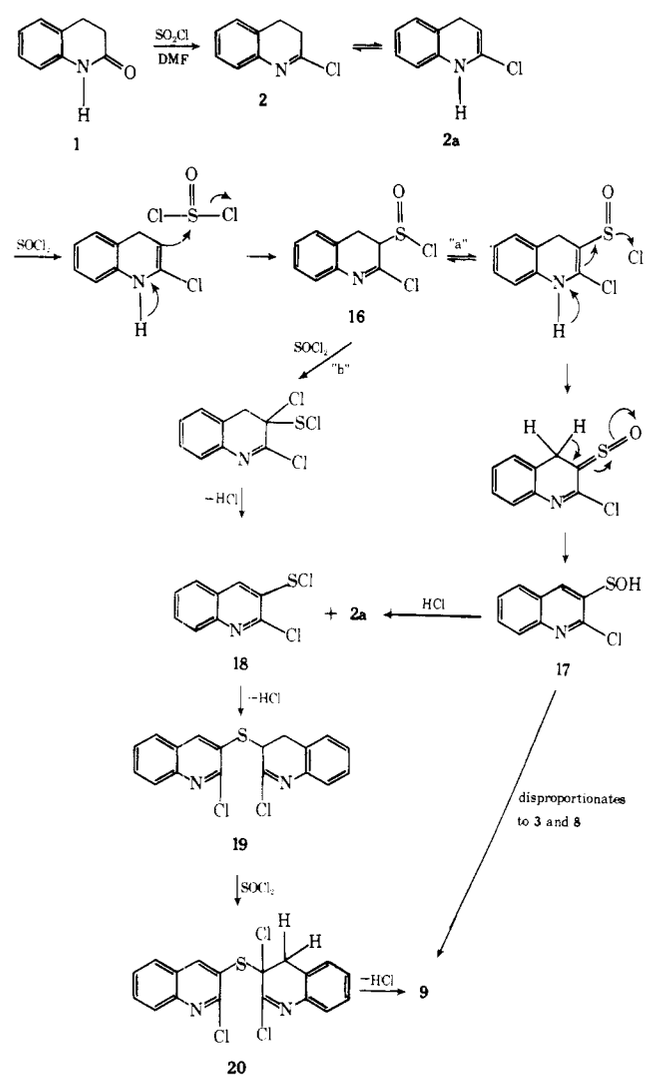
Since Oka et al. did not report disulfide formation, it is difficult to assess the role of sulfur dichloride in these reactions. We wish to propose an alternative mechanism involving only thionyl chloride to explain the formation of both the disulfide **3** and the sulfide **9** (Scheme III). The imidoyl chloride **2** probably forms as expected[7] and then isomerizes to the enamine form **2a**,[8] which reacts with thionyl chloride in the manner shown to form the sulfinyl chloride **16**. Intermediate **16** loses hydrochloric acid to form the sulfenic acid **17** (route a). Sulfenic acids are known to undergo disproportionation[9] to disulfides and mercaptans, and this would explain the formation of **3** and **8**. Intermediate **17** could also react with hydrochloric acid to form sulfenyl chloride **18**, which could react with **2a** to form the sulfide **19** which could be chlorinated to **20**, followed by loss of hydrochloric acid to form **9**. Alternately, **18** could be formed directly by the reaction of sulfenyl chloride **16** with an additional mole of thionyl chloride (route b).[10]

Similarly, the reaction of mercaptan **8** with itself at high temperatures offers an explanation for the formation of **10a**,

Scheme II



Scheme III



while the reaction of **9** with sulfur or hydrogen sulfide, both of which are present in hot thionyl chloride,[2] could account for the small amount of **10b** in the reaction.

Experimental Section

Melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. Proton magnetic spectra were obtained on a Varian T-60 spectrometer, infrared spectra on a Perkin-Elmer Model 267 grating infrared spectrophotometer, and mass spectra on a consolidated Electrodynamics Corp. Model 2H10 mass spectrometer.

3,3′-Dithiobis(2-chloroquinoline) (3). To a solution of 14.7 g (0.1 mol) of 3,4-dihydro-2(1*H*)-quinolinone (**1**) in 100 mL of anhydrous dimethylformamide at 0–5 °C was added portionwise 36 g (0.30 mol) of thionyl chloride; the temperature of the reaction was kept below 15 °C throughout the addition. The reaction was allowed to stir for 2 h and then filtered through a sintered glass filter. The off-white precipitate which collected was washed with 25 mL of DMF and recrystallized from butanol: yield 8.7 g (45%); mp 242 °C; mass spectrum, *m/e* 389 (M^+); NMR (deuteriotrifluoroacetic acid) δ 9.4 (s, 2), 8.1–8.4 (m, 8, aromatic).

Anal. Calcd for $C_{18}H_{10}Cl_2N_2S_2$: C, 55.53; H, 2.59; N, 7.21; S, 16.47; Cl, 18.21. Found: C, 55.81; H, 2.64; N, 7.32; S, 16.24; Cl, 18.43.

3,3′-Thiobis(2-chloroquinoline) (9). The DMF filtrate from the above reaction was poured into 500 mL of water, and a yellow solid precipitated which was isolated by filtration and fractionally crystallized from methanol to yield 4.2 g (23%) of **9**: mp 198–200 °C; mass spectrum, *m/e* 356 (M^+); (deuteriotrifluoroacetic acid) δ 9.23 (s, 2), 8.08–8.45 (m, 8, aromatic).

Anal. Calcd for $C_{18}H_{10}Cl_2N_2S$: C, 60.52; H, 2.82; N, 7.84. Found: C, 60.42; H, 2.80; N, 7.74.

2-Chloro-3-(methylthio)quinoline (5). A slurry of 2.0 g (0.0054 mol) of disulfide **3** in 150 mL of 95% ethanol was heated to reflux. To the refluxing slurry was added, portionwise, 4.0 g (0.105 mol) of sodium borohydride (Alfa Products). The mixture was then refluxed for 30 min, at which point complete solution was obtained. To this solution was added 10 g (0.07 mol) of methyl iodide and the solution was refluxed overnight. The solvent was removed in vacuo and the dry residue was slurried with water and filtered. The product was recrystallized from ethanol/water to yield 1.3 g: mp 107–108 °C; NMR (deuteriochloroform) δ 7.2–8.1 (m, 5, aromatic), 2.46 (s, 3, methyl).

Anal. Calcd: C, 57.28; H, 3.58; N, 6.68; Cl, 16.91; S, 15.29. Found: C, 57.28; H, 3.97; N, 6.43; Cl, 17.20; S, 15.32.

4-(Methylthio)tetrazolo[1,5-*a*]quinoline (6). To a solution of 1.3 g (0.006 mol) of 2-chloro-3-(methylthio)quinoline (**5**) in 25 mL of 95% ethanol was added a saturated solution of 1.0 g of sodium azide in a minimum amount of water. This solution was refluxed and to it was added 2 mL of a 10% hydrochloric acid solution. The stirred solution was refluxed for 3 h, cooled, poured into 200 mL of cold water, filtered, and recrystallized from ethanol: yield 0.8 g; mp 163–167 °C; NMR (deuteriochloroform) δ 8.5–8.76 (m, 1), 7.6–8.1 (m, 4, aromatic), 2.9 (s, 3-CH_3).

4-(Methylthio)tetrazolo[1,5-*a*]quinoline (6). Excess methyl mercaptan was bubbled into a solution of 1.9 g of sodium in 200 mL of anhydrous ethanol for 45 min. To this solution was added 5.0 g (0.025 mol) of 4-chlorotetrazolo[1,5-*a*]quinoline[11] (**7**), and the stirred reaction was refluxed for 12 h. The solvent was removed, and the solid remaining was taken up in 10% ethyl acetate in toluene and eluted through a silica gel column. Two materials were isolated. The first (1.2 g, 22% yield) was identical with the 4-(methylthio)tetrazolo[1,5-*a*]quinoline isolated from the previous reaction.

The second material proved to be the 5-(methylthio)-tetrazolo[1,5-*a*]quinoline when compared to authentic material.

Quinolino[2,3-*b*]-1,4-dithiino[5,6-*b*]quinoline (10a) and Quinolino[2,3-*b*]-1,4-dithiino[2,3-*b*]quinoline (10b). To a solution of 7.35 g (0.05 mol) of **1** in 100 mL of anhydrous DMF, heated to 100 °C by means of a water bath, was added 18 g (0.15 mol) of thionyl chloride over a few minutes. An exothermic reaction occurred, and the temperature rose to 115 °C, turning dark red in the process. After 1 h at 100 °C, the reaction was cooled to 0 °C and filtered to yield 1.76 g (18%) of **3**. The filtrate was poured into water, and a yellow solid was isolated. This solid was placed on an alumina column and eluted with methylene chloride. The first of the two major materials isolated was **10a:** 2.15 g, 27%; R_f 0.65 (methylene chloride on alumina TLC plate); mp 287–289 °C; mass spectrum, *m/e* 318 (M^+); NMR (deuteriotrifluoroacetic acid) δ 9.25 (s, 2), 7.9–8.43 (m, 8, aromatic).

Anal. Calcd for $C_{18}H_{10}N_2S_2$: C, 67.90; H, 3.17; N, 8.80; S, 20.14. Found: C, 68.12; H, 3.06; N, 8.77; S, 19.84.

The second material was **10b:** 0.50 g, 6%; R_f 0.21 (methylene chloride on alumina TLC plate); mp 258–259 °C; mass spectrum, *m/e* 318 (M^+); NMR (deuteriotrifluoroacetic acid) δ 9.26 (s, 2), 7.94–8.45 (m, 8, aromatic).

Anal Calcd for $C_{18}H_{10}N_2S_2$: C, 67.90; H, 3.17; N, 8.80; S, 20.14. Found: C, 67.67; H, 3.43; N, 8.59; S, 19.86.

Quinolino[2,3-*b*]-1,4-dithiino[5,6-*b*]quinoline (10a). A solution of 1.6 g (0.0049 mol) of **3** in a minimum amount of butanol (200 mL) was prepared. To this was added 2.0 g (0.05 mol) of sodium borohy-

dride; a vigorous evolution of gas accompanied the addition. The solution went from clear to cloudy upon further refluxing. The reaction was refluxed for an additional hour, cooled, and filtered: yield (M^+) 1.2 g (91.0%); mp 285–287 °C; mass spectrum, *m/e* 318 (M^+). The infrared and NMR spectra were also identical with **10a.**

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Registry No.—**1,** 553-03-7; **3,** 68844-39-3; **5,** 68844-40-6; **6,** 68844-41-7; **7,** 35213-70-8; **8,** 68844-42-8; **9,** 68844-43-9; **10a,** 68844-44-0; **10b,** 68844-45-1; thionyl chloride, 7719-09-7; sodium azide, 26628-22-8.

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(10) This is similar to the mechanism proposed for the reaction of thionyl chloride with carboxylic acids: Arnold J. Krubsack and Tatsuo Higa, *Tetrahedron Lett.*, 5149–5152 (1968).
(11) B. A. Dreikorn. U.S. Patent 3 764 681 (1973).

"One-Pot" Construction of the Bithiopyran Ring System from an Acyclic Precursor

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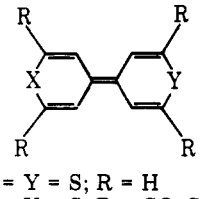
Synthetic procedures to derivatives of $\Delta^{4,4'}$-bithiopyran (BTP, **1a**), a ring system of interest to use in connection with

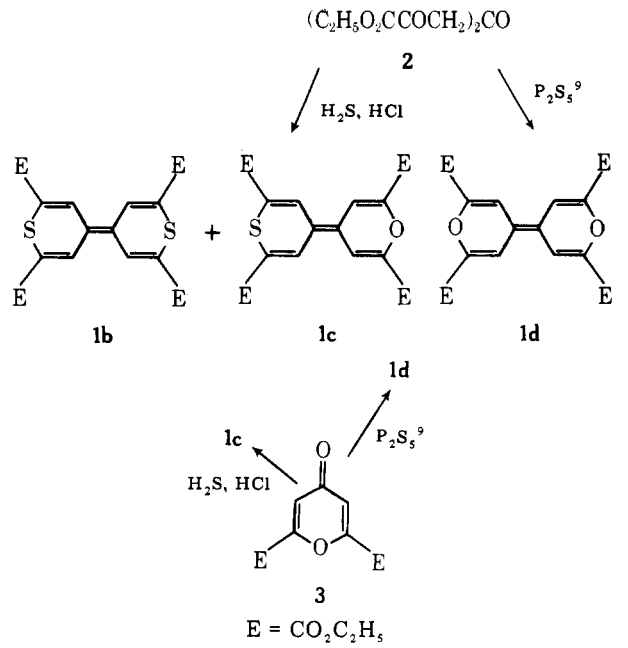


1a, X = Y = S; R = H
b, X = Y = S; R = $CO_2C_2H_5$
c, X = O; Y = S; R = $CO_2C_2H_5$
d, X = Y = O; R = $CO_2C_2H_5$
e, X = Y = O; R = H
f, X = Y = O; R = C_6H_5
g, X = Y = S; R = C_6H_5

our work on organic conductors,[1] and its benzannelated analogues typically involve a thiopyran derivative which is either reductively coupled[1-5] or induced to eliminate a chalcogen by either thermal[2,6] or photochemical[7] means. We now report the first procedure which yields a derivative of BTP from an acyclic precursor which does not contain sulfur.

When an ethanol solution of the readily available acetonedioxalic ester[8] (**2**) is treated with a mixture of hydrogen chloride and an excess of hydrogen sulfide in a Paar autoclave (Scheme I), the dark green 2,2′,6,6′-tetracarboethoxybi-

Scheme I

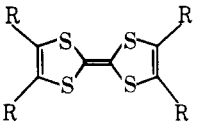


thiopyran (**1b**) is obtained in 60% yield after column chromatography. If the same reaction is carried out in conventional glassware at atmospheric pressure, a mixture of **1b** and the thiabipyran tetraester **1c**, a previously unknown ring system, is obtained. The known[9] bipyran tetraester **1d** could not be detected in these reaction mixtures by thin-layer chromatography (TLC). Further, **1d** is recovered unchanged from reaction mixtures which yield **1b** and **1c** and thus is not an intermediate in their formation. Moreover, diethyl chelidonate (**3**) reacts with H_2S and HCl to give a complex mixture from which **1c** may be isolated in ~10% yield. Thus, while **3** may be used to prepare **1c**, it is not useful for the preparation of **1b** and is not an intermediate in its synthesis.

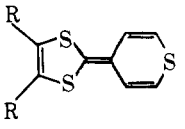
Table I lists the electrochemical and electronic spectral data for **1b, 1c,** and **1d,** along with the data for the unsubstituted compounds, **1a** and **1e,** and for the isoelectronic tetrathiafulvalene (TTF, **4**) and 2-(thiopyran-4-ylidene)-1,3-dithiole[10] (TPDT, **5**) derivatives.

The oxidation potentials ($E_{1/2}^{ox}$) of **1a** and **1e** are significantly increased by the introduction of four electron-attracting ester groups, as expected. This effect is somewhat bigger than that observed for the TTF derivatives **4a** and **4b.** The tetraester of BTP (**1b**) is more easily oxidized than the corresponding TTF tetraester **4b,** a trend found in the parent compounds.

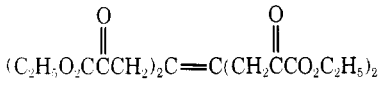
The major result of tetraester substitution on the absorption spectra of **1a** and **1e** is the shift of the major absorption band to longer wavelength. The effect is reminiscent of the behavior of phenyl substituents[4] in the same positions (**1f,g**). As with the electrochemical data, the absorption properties of **1c** are intermediate to those of **1b** and **1d.** While the major



4a, R = H
b, R = CO_2CH_3



5a, R = H
b, R = CO_2CH_3



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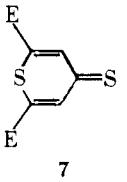

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