

# Synthesis of Some New Benzo[*b*]thiophene, Oxofluoreno[4,3-*b*]thiophene, Cyclic Hydrazides and Acridine Compounds

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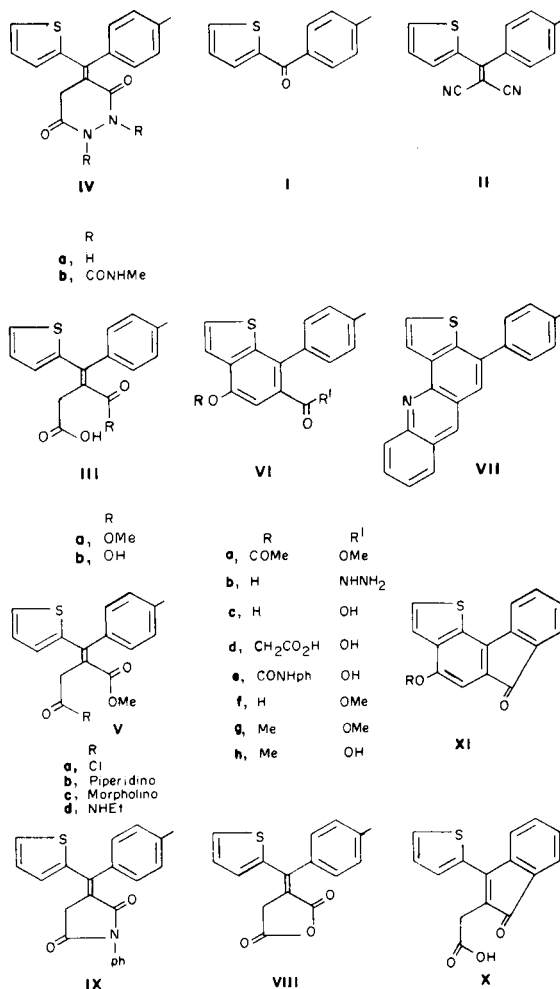
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*p*-Tolyl 2-thienyl ketone (I) condensed with dimethyl succinate in the presence of potassium *t*-butoxide to give the *trans* (SC<sub>4</sub>H<sub>3</sub>/CO<sub>2</sub>Me) half-ester (IIIa) whose configuration was deduced by cyclization to the corresponding benzo[*b*]thiophene derivatives. Carbamates, esters, cyclic hydrazides and substituted phenolic and acetic acids useful as antibacterial and antiinflammatory agents were obtained. The reaction of ketone I with malononitrile to give ylidene malononitrile II was also considered.

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The synthesis of benzo[*b*]thiophene by the Stobbe condensation has been reported (1). Here we describe analogous preparations as possible precursors of pharmacologically active compounds (2). *p*-Tolyl 2-thienyl ketone (I) condensed with dimethyl succinate in the presence of potassium *t*-butoxide in *t*-butyl alcohol to give the half-ester IIIa. The structure follows from both spectroscopic examination and chemical transformations. The affinity of ester IIIa and its corresponding diacid IIIb to react with hydrazine hydrate was fulfilled in ethanol to furnish cyclic hydrazide IVa. We thus prepared dicarbamate IVb by the hydrazide treatment with methyl isocyanate. Acid chloride Va, obtained by the action of thionyl chloride on IIIa, reacted with piperidine, morpholine and ethylamine to give Vb-d. Cyclization of IIIa with sodium acetate-acetic anhydride gave the respective methyl 7-(*p*-tolyl)-4-acetoxybenzo[*b*]thiophene-6-carboxylate (VIa) which showed well defined absorption bands for the acetoxy and ester groups in its ir spectrum. The electronic spectrum supports well the structure of *p*-tolylbenzo[*b*]thiophene. The nmr spectrum showed signals due to methyl resonance. The structure of the acetoxy ester VIa was well established by the following series of reactions; it reacted readily with hydrazine hydrate to form the hydroxy hydrazide VIIb, inferred by spectral and analytical data. The preparation of arylóxyacetic acid VIc and carbamate VIe known for their activity are the subject assigned to our laboratory. The phenolic acid VIc suitable for their formation was obtained by saponification of ester VIa. Esterification of the phenolic acid VIc was verified with methanol and dry hydrogen chloride gas. The phenolic ester VIe, which was obtained gave hydrazide VIIb when treated with hydrazine hydrate. Its identity was established by direct comparison (mmp) with the product obtained by the hydrazine treatment of VIa. The hydroxy acid VIc was converted with dimethyl sulphate and potassium carbonate in acetone into the respective methoxy ester VIg. Saponification and

subsequent decarboxylation gave the corresponding 4-methoxy-7-(*p*-tolyl)benzo[*b*]thiophene, the structure of which follows from its cleavage with hydriodic acid to its corresponding hydroxybenzo[*b*]thiophene, which exhibited only one strong band at 800 cm<sup>-1</sup> for the two adja-



cent H-atoms in its spectrum in addition to the phenolic band at  $3410\text{ cm}^{-1}$ .

Since we already have the 7-(*p*-tolyl)-4-hydroxybenzo[*b*]thiophene, we thought it interesting as a key intermediate in the synthesis of the acridine, which may be of biological value in view of its structural analogy with the known carcinogenic polycyclic acridines (3). When treated with aniline and paraformaldehyde, the hydroxybenzo[*b*]thiophene gave an orange product with no characteristic absorption bands in the ir spectrum. A low intensity absorption maxima appeared in the visible region at 410 nm which is due to  $n \rightarrow \pi^*$  transition (R-band). The analytical data agreed well with acridine VII. The methoxy acid VIh was cyclized by phosphorus pentoxide in dry benzene to give 4-methoxy-8-methyl-6-(*H*)oxofluoreno[4,3-*b*]thiophene. The structure assigned was supported by its red colour which is reflected in the electronic spectrum which showed absorption maximum at 470 nm due to the  $n \rightarrow \pi^*$  transition (R-band). The ir spectrum showed a strong band at  $1705\text{ cm}^{-1}$  characteristic of  $\nu\text{ C=O}$  of fluorenones. The dibasic acid IIIb was converted into its anhydride VIII which exhibited the expected carbonyl coupling bands in its ir spectrum. When treated with aniline in dioxane, the anhydride afforded anilide IX assigned by ir spectrum and analytical data. The same anhydride was treated with anhydrous aluminium chloride in nitrobenzene to give the indenylacetic acid X. The structure of this compound follows from the following evidence: its orange colour, solubility in sodium carbonate solution, formation of a 2,4-dinitrophenylhydrazone and the appearance of a broad infrared band at  $1710\text{--}1700\text{ cm}^{-1}$  for  $\nu\text{ C=O}$  of the  $\alpha,\beta$ -unsaturated five membered cyclic ketones and aliphatic acids. The orange colour was reflected in the appearance of a low intensity absorption maximum in the visible region at 417 nm, which is due to  $-\pi^*$  transition (R-band).

## EXPERIMENTAL

Melting points are uncorrected. Ir spectra (potassium bromide,  $\nu$  max in  $\text{cm}^{-1}$ ) were recorded on a Beckman IR 4220 spectrophotometer and electronic spectra (methanol,  $\lambda$  max in nm) on a Beckman UV 5230 spectrophotometer. The nmr spectra were determined in deuteriochloroform at a frequency of 60 MHz on Varian EM-360 spectrometer using tetramethyl silane as an internal standard. The peak positions are expressed in ppm ( $\delta$ ).

$\alpha$ -Cyano- $\beta$ -(2-thienyl)- $\beta$ -(*p*-tolyl)acrylonitrile (II).

A solution of ketone I (0.15 mole), malononitrile (0.25 mole), 6 g of ammonium acetate and 12 ml of glacial acetic acid in 100 ml of toluene was refluxed with the aid of a Dean-Stark trap until the amount of water collected in the trap remained constant (30 hour). The solution was then cooled and decanted from malononitrile polymer. The polymeric gum was washed with toluene and the combined toluene fractions were washed with water and dried over anhydrous sodium sulphate. After concentration the resulting residue was crystallized from methanol giving pale yellow crystals (24%), mp  $103\text{--}105^\circ$ ; ir:  $2230\text{ cm}^{-1}$  (CN).

Anal. Calcd. for  $\text{C}_{13}\text{H}_{10}\text{N}_2\text{S}$ : C, 72.0; H, 4.0; N, 11.2; S, 12.8. Found: C,

72.3; H, 4.2; N, 10.9; S, 12.6.

*trans*-( $\text{SC}_6\text{H}_4\text{CO}_2\text{Me}$ )-3-Methoxycarbonyl-4-(*p*-tolyl)-4-(2'-thienyl)but-3-enoic Acid (IIIa) and its Corresponding Dibasic Acid (IIIb).

A mixture of *p*-tolyl 2-thienyl ketone (0.1 mole) and dimethyl succinate (0.12 mole) in 20 ml of *t*-butyl alcohol was gradually added during 30 minutes to a cold and stirred solution of potassium *t*-butoxide (from 4 g of metallic potassium and 80 ml of *t*-butyl alcohol). The mixture was heated for a further 1 hour and thereafter worked up as usual (4). Acidification of the bicarbonate extracts afforded the oily half-ester (IIIa, 92%); ir:  $1705\text{ cm}^{-1}$  (C=O, ester). Saponification with 10% aqueous sodium hydroxide gave a pale brown viscous oil. This was triturated with *n*-hexane to give white needles of IIIb, mp  $154\text{--}156^\circ$  from ether-*n*-hexane (77%); ir:  $1690\text{ cm}^{-1}$  (C=O).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{S}$ : C, 63.5; H, 4.6; S, 10.5. Found: C, 63.2; H, 4.5; S, 10.9.

Oxidation of the Half-Ester (IIIa).

To the solution of 2 g of IIIa in 20 ml of 20% sodium carbonate solution, 45 ml of 2% potassium permanganate solution was added dropwise while stirring until the colour persisted. The reaction mixture was left for 2 hours at room temperature then extracted with ether. The ether layer was washed with water, dried over anhydrous sodium sulphate and evaporated to give *p*-tolyl 2-thienyl ketone, mp and mixed mp  $68\text{--}72^\circ$ .

Reaction of IIIa with Hydrazine Hydrate. Formation of IVa.

To the solution of 1 g of IIIa in 20 ml of absolute ethanol, 1 ml of hydrazine hydrate was added. The reaction mixture was heated for 30 minutes then left over night. Ethyl alcohol was removed under reduced pressure. The precipitated product was filtered off and crystallized from methanol giving 0.4 g (42%) of IVa in shiny colourless crystals, mp  $179\text{--}182^\circ$ ; ir:  $3305\text{ (NH)}$  and  $1625\text{ (C=O)}$ .

Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ : C, 64.4; H, 4.6; N, 9.4; S, 10.7. Found: C, 64.6; H, 4.4; N, 8.8; S, 11.2.

Reaction of IIIb with Hydrazine Hydrate. Formation of IVa.

To a hot solution of 1 g of IIIb in 20 ml of absolute ethanol, 1 ml of hydrazine hydrate in 10 ml of absolute ethanol was gradually added dropwise with shaking. The precipitated white product was left for 2 hours, cooled, filtered and crystallized from methanol giving 0.7 g (71%) of IVa in shiny colourless crystals, mp  $182\text{--}184^\circ$ , on mixing with a sample obtained by the hydrazine treatment of IIIa, the mp was not depressed. The ir spectral bands for both were identical.

Reaction of IVa with Methyl Isocyanate. Formation of IVb.

A solution of 1.5 g of IVa, 0.3 ml of methyl isocyanate and 2 drops of triethylamine in dry benzene (10 ml) was heated under reflux for 5 hours. The solution was evaporated to dryness and the oily residue was washed with benzene several times and crystallized from acetic acid giving 1.2 g (60%) of the dicarbamate as colourless crystals, mp  $243\text{--}245^\circ$ ; ir:  $3310, 1710$  and  $1675$ .

Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_4\text{S}$ : C, 58.2; H, 4.8; N, 13.6; S, 7.7. Found: 58.3; H, 5.1; N, 13.2; S, 8.1.

Preparation of Acid Chloride Va.

Thionyl chloride (100 ml) was added to 6 g of the half-ester IIIa and warmed on water bath for 2 hours. After removal of thionyl chloride, the resulting residue was used directly for the preparation of the corresponding amides.

Preparation of Amides Vb-d.

To a solution of 2 g of acid chloride Va in 50 ml of dry benzene, 2 g of piperidine, morpholine or ethylamine was added. The mixture was heated on a boiling water bath for 1 hour. After cooling, the precipitate which was obtained crystallized from the proper solvent.

Piperidino Derivative Vb.

This compound was obtained in a yield of 39% (0.9 g) from methanol,

mp 207-209°; ir: 1735 and 1705 (C=O).

*Anal.* Calcd. for  $C_{22}H_{23}NO_3S$ : C, 68.9; H, 6.5; N, 3.6; S, 8.4. Found: C, 69.2; H, 6.4; N, 3.8; S, 8.8.

#### Morpholino Derivative Vc.

This compound was obtained in a yield of 46% (1.1 g) from methanol, mp 191-192°; ir: 1745 and 1710 (C=O).

*Anal.* Calcd. for  $C_{21}H_{23}NO_4S$ : C, 65.5; H, 5.9; N, 3.6; S, 8.3. Found: C, 65.8; H, 5.5; N, 4.1; S, 7.8.

#### N-Ethylamido Derivative Vd.

This compound was obtained in a yield of 38% (0.8 g) from benzene, mp 220-223°; ir: 3280 (NH), 1710 and 1655 (C=O).

*Anal.* Calcd. for  $C_{19}H_{21}NO_3S$ : C, 66.4; H, 6.1; N, 4.1; S, 9.3. Found: 66.2; H, 5.9; N, 3.9; S, 9.8.

#### Methyl 7-(*p*-Tolyl)-4-acetoxybenzo[*b*]thiophene-6-carboxylate (VIa).

A mixture of 5 g of IIIa and 3 g of freshly fused sodium acetate in 30 ml of acetic anhydride was refluxed for 6 hours and the neutral cyclization product was isolated in the usual manner (4) to give 4.6 g (82%) of acetoxy ester VIa, mp 105° from methanol; ir: 1765 and 1710 (C=O in the acetoxy and the ester groups, respectively); uv: 240, 273 and 307 ( $\epsilon$ , 23000, 9000 and 7000);  $\delta$  (deuteriochloroform): 2.45 (3H, s, -COCH<sub>3</sub> at C-4) 2.6 (3H, s, CH<sub>3</sub>-ph), 3.65 (3H, s, -COOCH<sub>3</sub> at C-6). The spectrum is very complex in the aromatic region due to the superimposition of the signals of phenylbenzo[*b*]thiophene.

*Anal.* Calcd. for  $C_{19}H_{18}O_5S$ : C, 67.1; H, 4.7; S, 9.4. Found: C, 66.8; H, 4.6; S, 9.8.

#### Reaction of VIa with Hydrazine Hydrate. Formation of VIb.

To a solution of 1 g of VIa in 30 ml of absolute ethanol, 1 ml of hydrazine hydrate was added. The reaction mixture was heated for 5 minutes and left overnight. The solid obtained was crystallized from methanol to give 0.45 g (51%) of VIb, mp 179-181°; ir: 3410 (OH, broad), 3300 (NH), 3150 (NH<sub>2</sub>) and 1665 (C=O).

*Anal.* Calcd. for  $C_{16}H_{14}N_2O_2S$ : C, 64.4; H, 4.7; N, 9.3; S, 10.7. Found: C, 64.5; H, 4.5; N, 8.9; S, 11.2.

#### 7-(*p*-Tolyl)-4-hydroxybenzo[*b*]thiophene-6-carboxylic Acid (VIc).

The acetoxy ester VIa (4 g) was boiled with aqueous alcoholic potassium hydroxide (5% v/v, 80 ml) for 3 hours. The alkaline solution was filtered, acidified, extracted with ether and dried over anhydrous sodium sulphate. After removal of the ether, the resulting pale brown oil was triturated with *n*-hexane giving 3.1 g (93%) of white crystals, mp 157-158° from ether-*n*-hexane; ir: 3410 (OH, broad) and 1692 (C=O); uv: 240, 270 and 300 ( $\epsilon$ , 20000, 8000 and 7000).

*Anal.* Calcd. for  $C_{16}H_{12}O_3S$ : C, 67.6; H, 4.2; S, 11.2. Found: C, 67.5; H, 4.3; S, 11.5.

#### 7-(*p*-Tolyl)benzo[*b*]thiophene-6-carboxy-4-oxycetic Acid (VID).

To a mixture of 1 g of the phenolic acid and 3.5 ml of 33% aqueous sodium hydroxide, 2.5 ml of 50% chloroacetic acid solution was added and heated for 1 hour. The mixture was then cooled, diluted and acidified to give 0.5 g (42%) of white crystals, mp 207-209° from acetic acid; ir: 1705 (C=O); uv: 242, 270 and 310 ( $\epsilon$ , 26000, 12000 and 8000).

*Anal.* Calcd. for  $C_{18}H_{14}O_5S$ : C, 63.1; H, 4.1; S, 9.4. Found: C, 62.9; H, 4.2; S, 9.7.

#### 7-(*p*-Tolyl)-4-phenylcarbamatebenzo[*b*]thiophene-6-carboxylic Acid (VIe).

The phenolic acid VIc (2 g) was dissolved in 5 ml of dry benzene, 1 ml of phenyl isocyanate was then added followed by 2 drops of triethylamine. The reaction mixture was warmed for 1 hour, cooled and left for 2 hours in dry conditions. The product precipitated, was filtered off and was crystallized from benzene giving 1.1 g (39%) of the carbamate VIa, mp 173-176°; ir: 3240 (NH), 1710 and 1685 (C=O).

*Anal.* Calcd. for  $C_{22}H_{17}NO_3S$ : C, 68.4; H, 4.2; N, 3.5; S, 7.9. Found: C, 68.7; H, 3.9; N, 3.8; S, 8.3.

#### Methyl 7-(*p*-Tolyl)-4-hydroxybenzo[*b*]thiophene-6-carboxylate (VIc).

To a cold solution of 3 g of the phenolic acid (VIc) in 30 ml of absolute methanol, a dry current of hydrogen chloride gas was passed during 2 hours. The reaction mixture was left overnight. Methanol was then removed under reduced pressure. The product was extracted with ether, sodium bicarbonate solution and dried over anhydrous sodium sulphate. Ether was removed and the product obtained was crystallized from methanol giving 2.2 g (71%) of the phenolic ester VIc, mp 136-139°; ir: 3390 (OH, broad) and 1705 (C=O).

*Anal.* Calcd. for  $C_{17}H_{14}O_3S$ : C, 68.4; H, 4.6; S, 10.7. Found: C, 68.7; H, 4.6; S, 10.3.

#### Methyl 7-(*p*-Tolyl)-4-methoxybenzo[*b*]thiophene-6-carboxylate (VIg).

The phenolic acid VIc (2 g), dimethyl sulphate (6 g) and 8 g of anhydrous potassium carbonate in 50 ml of acetone were refluxed for 10 hours and the neutral product isolated in the usual manner (4). The ester was precipitated with light petroleum and crystallized from methanol giving 1.2 g (54%) of VIg, mp 93-94°; ir: 1717 (C=O).

*Anal.* Calcd. for  $C_{18}H_{16}O_3S$ : C, 69.2; H, 5.1; S, 10.3. Found: C, 69.2; H, 5.2; S, 10.7.

#### 7-(*p*-Tolyl)-4-methoxybenzo[*b*]thiophene-6-carboxylic Acid (VIh).

The methoxy ester VIg (2 g) was refluxed for 3 hours with 20 ml of 5% alcoholic potassium hydroxide. The alkaline solution was filtered and acidified. The methoxy acid VIh so obtained, (1.4 g, 73%) was crystallized from methanol in colourless crystals, mp 223-225°; ir: 1700 (C=O).

*Anal.* Calcd. for  $C_{17}H_{14}O_3S$ : C, 68.4; H, 4.6; S, 10.7. Found: C, 68.6; H, 4.4; S, 11.2.

#### 7-(*p*-Tolyl)-4-methoxybenzo[*b*]thiophene.

A solution of 2 g of the methoxy acid VIh in 10 ml of freshly distilled quinoline was treated with 1 g of copper-bronze and heated at 130° (sand-bath) for 1 hour. The reaction was worked up in the usual manner (4), affording 1.1 g (65%) of 7-*p*-tolyl-4-methoxybenzo[*b*]thiophene, mp 86° from methanol.

*Anal.* Calcd. for  $C_{16}H_{14}OS$ : C, 75.6; H, 5.5; S, 12.6. Found: C, 75.4; H, 5.3; S, 12.8.

#### 7-(*p*-Tolyl)-4-hydroxybenzo[*b*]thiophene.

The preceding methoxybenzo[*b*]thiophene (1.5 g) on boiling with hydriodic acid (60 ml) for 1 hour, gave after cooling a residue which was purified through its sodium salt and crystallized from water to give 0.8 g (57%) of the corresponding hydroxybenzo[*b*]thiophene as pale yellow glistening needles, mp 118-121°; ir: 3410 and 800  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{15}H_{12}OS$ : C, 75.0; H, 5.0; S, 13.3. Found: C, 75.4; H, 5.1; S, 13.8.

#### Fetvadjan Ullmann Reaction.

A mixture of 1 ml of freshly distilled aniline and 1 g of 7-(*p*-tolyl)-4-hydroxybenzo[*b*]thiophene was brought to the boiling point and 0.3 g of paraformaldehyde was added in small portions. Heating was continued with stirring until a homogenous liquid was obtained (15 minutes). After cooling the mass obtained was pulverised and purified *via* the picrate, which was crystallized from nitrobenzene. Basification with ammonia furnished a solid which was recrystallized from benzene-toluene to give 0.2 g (15%) of the acridine VII as an orange product, mp 237-239°. The picrate formed, mp over 300°; uv: 283, 307, 350 and 455 ( $\epsilon$ , 32000, 23000, 4000 and 1000).

*Anal.* Calcd. for  $C_{22}H_{15}NS$ : C, 81.2; H, 4.6; N, 4.3; S, 9.8. Found: C, 80.4; H, 4.5; N, 4.6; S, 10.2.

#### *trans*-(SC<sub>6</sub>H<sub>3</sub>/CO<sub>2</sub>H)-3-Carboxy-4-(*p*-tolyl)-4-(2'-thienyl)but-3-enoic Acid Anhydride (VIII).

The dibasic acid IIIb (4 g) was boiled with 40 ml of acetyl chloride for 2 hours. Acetyl chloride was removed under reduced pressure and the remaining residue was crystallized from benzene to give 3.1 g (82%) of the corresponding anhydride as yellow needles, mp 114-116°; ir: 1830 and

1770 (C=O).

*Anal.* Calcd. for  $C_{16}H_{12}O_3S$ : C, 67.7; H, 4.2; S, 11.2. Found: C, 68.1; H, 4.2; S, 10.9.

#### Reaction of Anhydride VIII with Aniline. Formation of IX.

Solutions of 1 g of distilled aniline and 1 g of the anhydride VIII in 10 ml of dioxane were mixed and heated for 30 minutes on a steam bath. On cooling and trituration with *n*-hexane, the resulting residue was crystallized from benzene-light petroleum giving 0.5 g (41%) of IX, mp 141-143°; ir: 1780 and 1710 (C=O).

*Anal.* Calcd. for  $C_{22}H_{17}NO_2S$ : C, 73.5; H, 4.7; N, 3.8; S, 8.9. Found: C, 73.5; H, 4.4; N, 3.4; S, 8.5.

#### 3-(2'-Thienyl)-3-(*p*-tolyl)-1*H*-oxo-2-indenylacetic Acid (X).

To the cold and stirred mixture of 3 g of anhydrous aluminium chloride in 25 ml of nitrobenzene, 6 g of the anhydride VIII was gradually added at such a rate that the temperature did not exceed 5°. The temperature was kept at that temperature for 3 hours, then at room temperature for 2 days with occasional stirring. The product was decomposed and the nitrobenzene was steam distilled. The residue was extracted with alkali and the extracts washed with ether and acidified. The product was filtered off, washed with cold water, dried and crystallized from benzene to give 4.4 g (73%) of orange crystals, mp 185-186°; ir: 1710 and 1700 (C=O); uv: 252, 300 and 417 ( $\epsilon$ , 32000, 9000 and 900).

*Anal.* Calcd. for  $C_{16}H_{12}O_3S$ : C, 67.6; H, 4.2; S, 11.3. Found: C, 67.5; H, 4.2; S, 11.6.

The 2,4-dinitrophenylhydrazone separated in red crystals, mp 227-230° from acetic acid.

*Anal.* Calcd. for  $C_{22}H_{16}N_4O_6S$ : N, 12.1. Found: N, 11.6.

#### 4-Methoxy-8-methyl-6*H*-oxofluoreno[4,3-*b*]thiophene (XI).

The solution of 1 g of the methoxy acid VIIh in 30 ml of dry benzene was treated with 5 g of phosphoric oxide and refluxed for 2 hours. Benzene was removed under reduced pressure and the residue was cooled and decomposed with water. The red product obtained was filtered off, washed with sodium carbonate solution then with water and crystallized from benzene to give 0.5 g (55%) of XI, mp 233-235°; ir: 1705 (C=O); uv: 277, 300, 350 and 470 ( $\epsilon$ , 34000, 32000, 4000 and 1000).

*Anal.* Calcd. for  $C_{17}H_{12}O_2S$ : C, 72.8; H, 4.3; S, 11.4. Found: C, 73.1; H, 4.3; S, 11.8.

The 2,4-dinitrophenylhydrazone separated in dark red crystals from xylene, mp 266-269°.

*Anal.* Calcd. for  $C_{23}H_{16}NO_5S$ : N, 12.1. Found: N, 12.4.

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