The Coupling of Thieno[3,2-*b*]thiophen-2-ones with Diazoalkanes

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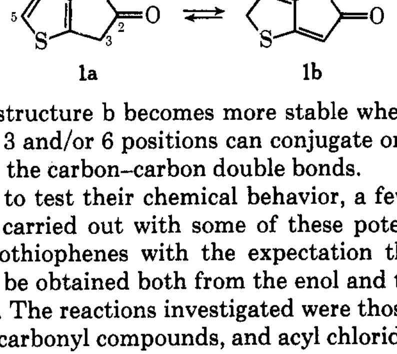
Thieno[3,2-*b*]thiophen-2(3*H*)-one reacted with diazoethane, in ether, to give the 3-ethylhydrazone of the thieno[3,2-*b*]thiophene-2,3-dione, the 2-ethoxythieno[3,2-*b*]thiophene, and the 3,3′-diethylthieno[3,2-*b*]thiophen-2-one; the hydrazone can further react with diazoalkanes to give the 2-alkoxy-3-ethylazothieno[3,2-*b*]thiophene. Reaction of diazoethane with 3-methylthieno[3,2-*b*]thiophen-2(3*H*)-one afforded only 2-ethoxy-3-methylthieno[3,2-*b*]thiophene and 3-methyl-3′-ethylthieno[3,2-*b*]thiophene; the same two products were formed starting from the tautomeric 3-methylthieno[3,2-*b*]thiophen-2(5*H*)-one. The formation of the reaction products is tentatively explained assuming the intermediate presence of the ethyldiazonium 2-thieno[3,2-*b*]thiophenate ion pair; decomposition within the ion pair should lead to O-alkylation or C-alkylation products, while the electrophilic attack of the diazonium cation on the anion would ultimately produce the ethylhydrazone. Some reactions of thieno[3,2-*b*]thiophen-2-ones and thieno[2,3-*b*]thiophen-2-ones with benzoyl chloride and carbonyl compounds also showed the property of these compounds of giving derivatives of the enol form as well as condensation products owing to the presence of active methylene groups.

It has been shown that the 2-hydroxy derivatives of thieno[3,2-*b*]thiophene and of thieno[2,3-*b*]thiophene do not exist as enols but have the structure of thiolactones;[2] in the case of the [2,3-*b*] compound only the thieno[2,3-*b*]thiophen-2(3*H*)-one form could be identified while in the thieno[3,2-*b*]thiophene series an equilibrium exists between the two tautomeric structures thieno[3,2-*b*]thiophen-2(3*H*)-one (**1a**) and thieno[3,2-*b*]thiophen-2(5*H*)-one (**1b**). The equilibrium is strongly influenced by substituents; thus structure b becomes more stable when substituents in the 3 and/or 6 positions can conjugate or hyperconjugate with the carbon–carbon double bonds.

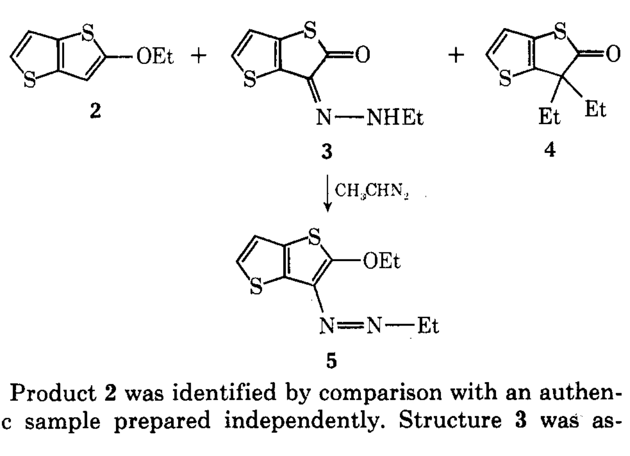


1a **1b**

In order to test their chemical behavior, a few reactions have been carried out with some of these potential 2-hydroxythienothiophenes with the expectation that derivatives could be obtained both from the enol and the thiolactone forms. The reactions investigated were those with diazoalkanes, carbonyl compounds, and acyl chlorides.

The reaction of **1a** with diazoethane in ether occurred smoothly at room temperature and afforded a mixture of compounds which could be separated by column chromatography. They were identified as 2-ethoxythieno[3,2-*b*]thiophene (**2**), thieno[3,2-*b*]thiophene-2,3-dione 3-ethylhydrazone (**3**), 3,3′-diethylthieno[3,2-*b*]thiophen-2-one (**4**), and 2-ethoxy-3-ethylazothieno[3,2-*b*]thiophene (**5**), which was formed in traces.

1a + CH_3CHN_2 ⟶



2 **3** **4** **5**

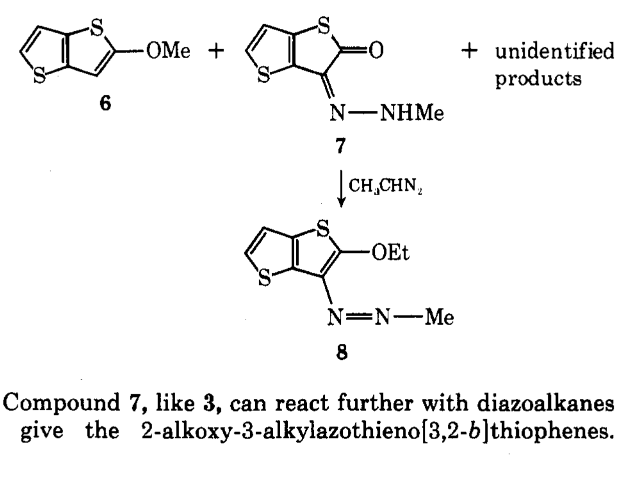
Product **2** was identified by comparison with an authentic sample prepared independently. Structure **3** was assigned to the main reaction product on the basis of its spectral and analytical data; the NMR spectrum in CS_2 showed a broad absorption at δ 11.25 (NH), two doublets at δ 7.18 and 6.83 ($J = 5.25$ Hz), respectively, due to the 5 and 6 protons of the thiophene ring, a quartet ($J = 7.25$ Hz) of doublets ($J = 4.5$ Hz) at δ 3.60 assigned to the CH_2 of the ethyl group, which is also coupled with the NH proton, and finally a triplet ($J = 7.25$ Hz) at δ 1.34 due to the CH_3 protons of the ethyl group; the infrared spectrum showed characteristic absorptions at 3220 ($\nu_{N\text{-}H}$) and at 1635 cm^{-1} ($\nu_{C=N} + \nu_{C=O}$) in agreement with the proposed structure.

The NMR spectrum of **4**, in CS_2, showed two doublets at δ 7.23 and 6.84 ($J = 5.25$ Hz) due to the two aromatic protons, a triplet (six hydrogens) at δ 0.7 ($J = 7.2$ Hz), and a complex spectral pattern (four hydrogens) centered at δ 1.75. This latter multiplet is ascribable to the methylenic protons which, being in nonequivalent environments, are diastereotopic; a complete analysis of the ABX_3 system was not attempted. A very similar multiplet is given by the methylene group of compound **11** described below.

As confirmed by independent synthesis, compound **5** forms through the reaction of **3** with excess diazoethane. Its structure is clearly demonstrated by the NMR spectrum, the chemical shifts of protons 5 and 6 being those expected for a thieno[3,2-*b*]thiophene derivative.[2,3]

Thieno[3,2-*b*]thiophen-2(3*H*)-one also reacts with diazomethane, but the separation of the reaction products is more difficult. The two main compounds formed from this reaction were 2-methoxythieno[3,2-*b*]thiophene (**6**) and thieno[3,2-*b*]thiophene-2,3-dione 3-methylhydrazone (**7**).

1a + CH_2N_2 ⟶

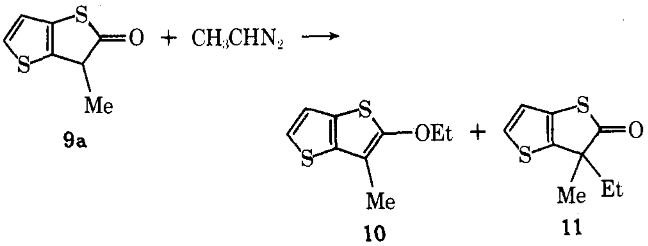


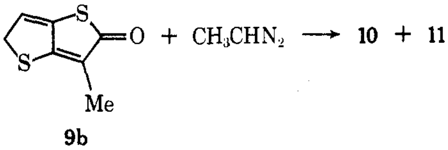
6 **7** **8**

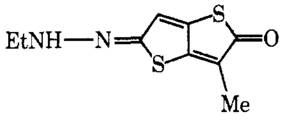
Compound **7**, like **3**, can react further with diazoalkanes to give the 2-alkoxy-3-alkylazothieno[3,2-*b*]thiophenes.

The treatment of **7** with diazoethane afforded 2-ethoxy-3-methylazothieno[3,2-*b*]thiophene (**8**).

Reaction of diazoethane with 3-methylthieno[3,2-*b*]thiophen-2(3*H*)-one (**9a**) gave only two products identified as 2-ethoxy-3-methylthieno[3,2-*b*]-thiophene (**10**) and 3-methyl-3′-ethylthieno[3,2-*b*]thiophen-2-one (**11**). Compound **11** showed a special NMR pattern due to two different geminal hydrogens in the ethyl group. This is expected on the basis of the proposed structure where the ethyl group is linked to a chiral center. The NMR spectrum at 60 MHz was rather complex in the methylene region, which was very similar to that of compound **4**; the NMR spectrum was also recorded at 100 MHz and the different δ and *J* values of the ABX_3 system were calculated by use of the standard LAOCOON 3 program. The same mixture of **10** and **11** was obtained when the tautomer 3-methylthieno[3,2-*b*]thiophen-2(5*H*)-one (**9b**) was treated with diazoethane, suggesting that the two reactions probably proceed through a common intermediate. No evidence could be found for the 5-ethylhydrazone **12**, which could be expected to form by analogy with the reaction of **1a**.







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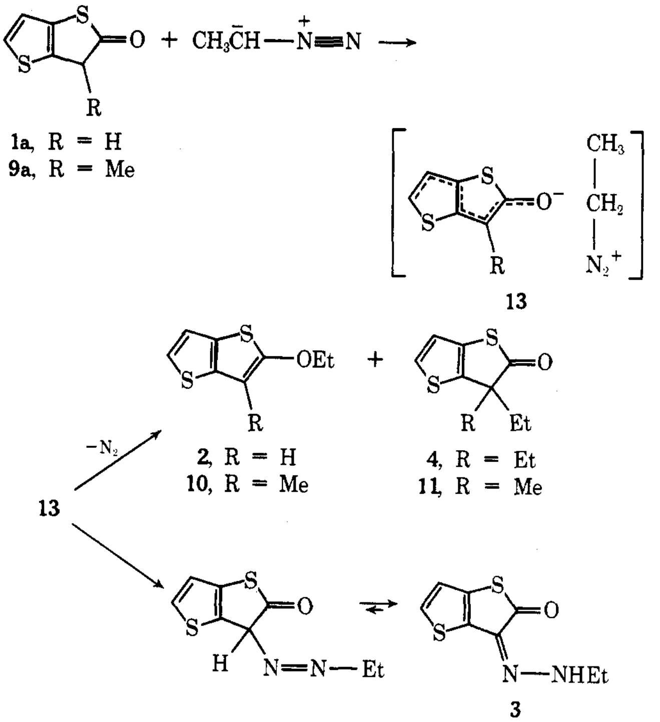
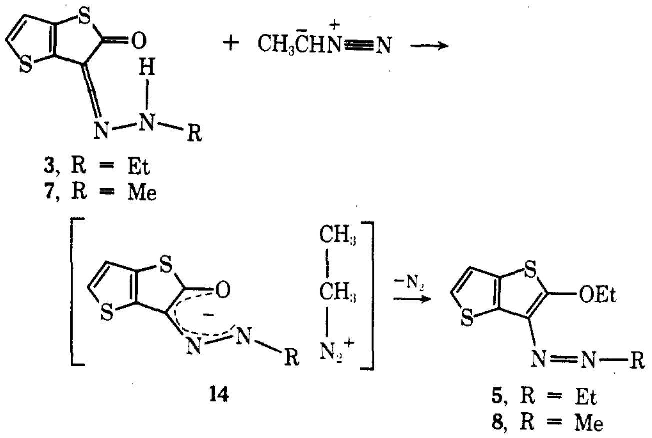
A rationalization of the experimental results assumes that, in the ethereal solvent in which these reactions take place, an interaction occurs between the basic diazoalkane and the acidic thieno[3,2-*b*]thiophen-2-one to afford an ion pair, **13**, constituted by alkyldiazonium cation and the mesomeric 2-thieno[3,2-*b*]thiophenate anion; this ion pair represents the intermediate from which the products originate. Decomposition within the ion pair should lead to the products of O- and C-alkylation with evolution of nitrogen, by nucleophilic attack of the bident anion on the carbon atom holding the diazo group; a similar mechanism was proposed by Huisgen and Rüchardt[4,5] to explain the reaction of benzoic acid with diazo-*n*-propane in ether. Another reaction path open to the ion pair is the electrophilic attack of the diazonium cation on the mesomeric anion; this is a coupling reaction which ultimately would lead to the hydrazones. Although the coupling of an aromatic diazonium salt with compounds bearing activated carbon–hydrogen bonds is well documented,[6] this reaction is very seldom encountered with aliphatic diazonium salts. Examples are, however, known of coupling of diazomethane with carbonyl activated methylenic groups.[7,8]

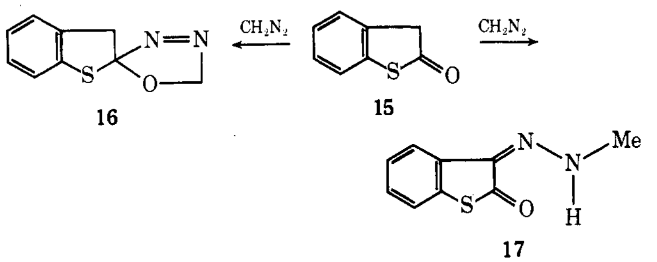
The same mesomeric anion, and hence the same ion pair **13**, should obviously result from the interaction of diazoethane with either **9a** or **9b**. C-Monoalkylation products were not isolated from the reaction of the unsubstituted compound **1a**, but the identification of compound **4** clearly indicates their intermediate formation; the 3-ethylthieno[3,2-*b*]thiophen-2(3*H*)-one is not very stable[2] and it probably decomposes during the several column chromatography operations necessary to effect a complete separation of the various components. Compounds **3** and **7** still contain an acidic hydrogen atom which can react with the diazoalkane to afford a new ion pair, **14**, to which only the O-alkylation path, which regenerates the aromaticity of the thienothiophene system, is now open and products **5** or **8** are obtained.



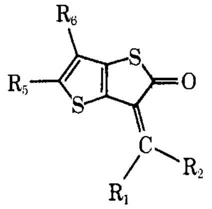


The coupling of the diazonium ion with the mesomeric anion and the C-alkylation reaction occur exclusively at the 3 position; position 5 is never involved. This is in agreement with greater electron density at the 3 than at the 5 position as determined by CNDO/2 calculations carried out on these anions.[2] As seen below, however, reactions do occur in the 5 position when attack at C-3 is blocked.

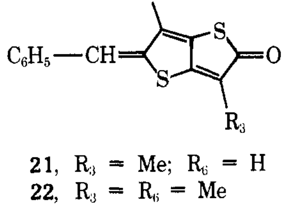
Conflicting results are reported in the literature concerning the structure of the reaction product of diazomethane and benzo[*b*]thiophen-2(3*H*)-one (**15**). Hawthorne and Porter[9] have reported the formation of the spirooxadiazoline **16**, while Schmiechen[8] has more recently suggested the hydrazone structure **17**. In the light of our results with thieno[3,2-*b*]thiophen-2-ones, the hydrazone structure seems more probable.



Reactions of the thieno[3,2-*b*]thiophene system with benzaldehyde and acetone led to compounds **18–22**.



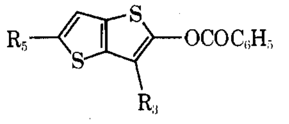
18, $R_1 = R_5 = R_6 = H$; $R_2 = C_6H_5$
19, $R_1 = R_2 = R_5 = Me$; $R_6 = H$
20, $R_1 = R_2 = Me$; $R_5 = H$; $R_6 = CMe_3$



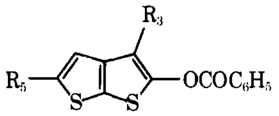
21, $R_3 = Me$; $R_6 = H$
22, $R_3 = R_6 = Me$

These compounds can be easily obtained in good yields by treating the solution of the appropriate thiolactone and acetone or benzaldehyde with gaseous hydrogen chloride; similar reactions were also given by the simpler thiolen-2-ones under the same experimental conditions.[10] Compounds **19** and **20** could also be obtained by simply passing 5-methylthieno[3,2-*b*]thiophen-2(3*H*)-one and 6-*tert*-butylthieno[3,2-*b*]thiophen-2(3*H*)-one, respectively, through an alumina column using a mixture of light petroleum and acetone as eluent. The condensations occur at the 3 position unless a substituent is present, in which case the reaction takes place at the 5 position, as is observed in compounds **21** and **22**.

Reactions which exclusively occur at the oxygen atom of the mesomeric anion are those with acyl chlorides which obviously afford the corresponding esters of the enol form; thus the 2-benzoyloxythieno[3,2-*b*]thiophenes or the 2-benzoyloxythieno[2,3-*b*]thiophenes can be conveniently obtained from the reaction of benzoyl chloride with an alkaline solution of the corresponding thienothiophen-2-ones. The following benzoyloxy derivatives, **23–28**, were prepared and characterized.



23, $R_3 = R_5 = H$
24, $R_3 = Me$; $R_5 = H$
25, $R_3 = H$; $R_5 = Me$



26, $R_3 = R_5 = H$
27, $R_3 = Me$; $R_5 = H$
28, $R_3 = H$; $R_5 = Me$

Experimental Section[11]

The thieno[3,2-*b*]thiophen-2(3*H*)-ones, thieno[3,2-*b*]thiophen-2(5*H*)-ones, and thieno[2,3-*b*]thiophen-2(3*H*)-ones were prepared as described in the previous paper.[2]

2-Methoxythieno[3,2-*b*]thiophene (6). A mixture of 2-bromothieno[3,2-*b*]thiophene[2] (1.95 g), sodium iodide (0.1 g), sodium methoxide (1.3 g), and CuO (0.35 g) in methanol (20 ml) was refluxed for 4 days; the solvent was distilled and the residue dissolved in ether and washed with water. The solvent was evaporated and the residue distilled to afford **6** (1 g): bp 80–81° (0.3 mm); NMR (CS_2) δ_{CH_3} 3.85, δ_3 6.29, δ_6 6.94, δ_5 7.03, $J_{5-6} = 5.25$, $J_{3-6} = 0.4$ Hz.

Anal. Calcd for $C_7H_6OS_2$: C, 49.38; H, 3.55; S, 37.66. Found: C, 49.17; H, 3.55; S, 37.66.

2-Ethoxythieno[3,2-*b*]thiophene (2). This compound was prepared as described above for **6** using sodium ethoxide and ethanol as solvent. The oily residue was chromatographed through a silica gel column using pentane as eluent. The desired product was obtained as a solid: mp 38–39°; NMR (CS_2) δ_{CH_3} 1.39, δ_{CH_2} 4.03, δ_3 6.28, δ_6 6.93, δ_5 6.96, $J_{CH_2CH_3} = 7.0$, $J_{5-6} = 5.25$ Hz, $J_{3-6} = 0.4$ Hz.

Anal. Calcd for $C_8H_8OS_2$: C, 52.14; H, 4.38; S, 34.80. Found: C, 52.31; H, 4.44; S, 34.54.

2-Ethoxy-3-methylthieno[3,2-*b*]thiophene (10). The synthesis of this compound was carried out as described above for compound **2**, starting from the 2-bromo-3-methylthieno[3,2-*b*]thiophene.[2] The desired product was purified by distillation: bp 108° (0.7 mm); NMR (CS_2) $\delta_{CH_2CH_3}$ 1.35, δ_{CH_3} 2.13, $\delta_{CH_2CH_3}$ 4.01, δ_6 6.95, δ_5 7.02, $J_{CH_2CH_3}$ 7.0, $J_{5-6} = 5.25$ Hz.

Anal. Calcd for $C_9H_{10}OS_2$: C, 54.51; H, 5.08; S, 32.34. Found: C, 54.81; H, 5.0; S, 32.11.

Reaction of Thieno[3,2-*b*]thiophen-2(3*H*)-one (1a) with Diazoethane. A solution of thieno[3,2-*b*]thiophen-2(3*H*)-one (**1a**, 4 g) and diazoethane (5.5 g) in ether was stirred at room temperature for 2 hr and the solvent evaporated. The residue was chromatographed through a silica gel column using a mixture of light petroleum and benzene (4:1) as eluent. The first fractions contained 2-ethoxythieno[3,2-*b*]thiophene (**2**, 0.6 g), identical with the authentic sample, and 3,3′-diethylthieno[3,2-*b*]thiophen-2-one (**4**, 0.4 g), bp 70–72° (0.3 mm); ir (CCl_4) 1720 cm^{-1} (C=O).

Anal. Calcd for $C_{10}H_{12}OS_2$: C, 56.57; H, 5.70; S, 30.20. Found: C, 56.37; H, 5.80; S, 30.10.

The complete separation of the two compounds was obtained after a second column chromatography.

The following fractions contained a mixture of compounds which could be separated by repeated column chromatography on silica gel using light petroleum–ether (9:1) as eluent; after this treatment 2-ethoxy-3-ethylazothieno[3,2-*b*]thiophene (**5**) was obtained as an oil (0.1 g), identical with the product prepared independently as described below. A second compound was then isolated (2.2 g) which was identified as thieno[3,2-*b*]thiophene-2,3 dione 3-ethylhydrazone (**3**), mp 101–102°, yellow needles from ethanol.

Anal. Calcd for $C_8H_8N_2OS_2$: C, 45.26; H, 3.80; N, 13.20; S, 30.22. Found: C, 45.16; H, 3.55; N, 12.94; S, 30.67.

The spectroscopic data for compounds **3** and **4** are reported in the text.

Reaction of Thieno[3,2-*b*]thiophen-2(3*H*)-one (1a) with Diazomethane. A solution of **1a** (0.8 g) and diazomethane (1.9 g) in ether was stirred at room temperature for 2 hr; an amorphous precipitate was formed which was insoluble in the usual organic solvents and which could not be identified. The filtered solution was evaporated and the residue chromatographed through a silica gel column using light petroleum–ether (9:1) as eluent. The first fractions contained 2-methoxythieno[3,2-*b*]thiophene (**6**, 0.1 g), identical with the authentic compound; the following fractions contained the yellow thieno[3,2-*b*]thiophen-2,3-dione 3-methylhydrazone (**7**, 0.4 g) which was purified by crystallization from ethanol: mp 119–120°; NMR (CS_2) δ_5 7.23, δ_6 6.90, δ_{CH_3} 3.41, δ_{NH} 11.18, $J_{5-6} = 5.25$, $J_{NH-CH_3} = 4.5$ Hz; ir (CCl_4) 3220 (NH), 1635 cm^{-1} (C=N, C=O).

Anal. Calcd for $C_7H_6N_2OS_2$: C, 42.4; H, 3.05; N, 14.13; S, 32.34. Found: C, 42.42; H, 3.06; N, 14.03; S, 32.26.

Reaction of 3-Methylthieno[3,2-*b*]thiophen-2(3*H*)-one (9a) with Diazoethane. A solution of **9a** (7 g) and diazoethane (4 g) in ether was stirred at room temperature for 3 hr and the solvent evaporated. The residue was chromatographed through a silica gel column to afford a first fraction containing two compounds and other fractions in which unidentified oily products were present. The two compounds present in the first fractions were separated by chromatography on Florisil using light petroleum as eluent. The first component was identified as 2-ethoxy-3-methylthieno[3,2-*b*]thiophene (**10**, 2.1 g) by comparison with the authentic compound. The second product was attributed the structure of 3-methyl-3′-ethylthieno[3,2-*b*]thiophen-2-one (**11**, 1.2 g): bp 76–77° (0.3 mm); ir (CCl_4) 1720 cm^{-1}; NMR (CS_2) δ_5 7.32, δ_6 6.93, δ_{CH_3} 1.40, $\delta_{CH_2CH_3}$ 1.83, 1.74, $\delta_{CH_2CH_3}$ 0.78, $J_{5-6} = 5.25$, $J_{CH_2CH_3}$ 7.4 Hz. (The ABX_3 system given by the ethyl group has been reconstructed for the spectrum recorded at 100 MHz. The following values accurately reproduced the experimental spectrum: δ_{Me} 73.92 ± 0.05 Hz, $\delta_{\mathrm{H_a}}$ 187.27 ± 0.034 Hz, $\delta_{\mathrm{H_b}}$ 167.74 ± 0.035 Hz, $J_{\mathrm{H_aX_3}}$ 7.18 ± 0.034 Hz, $J_{\mathrm{H_bX_3}} = 7.22 \pm 0.037$ Hz, $J_{\mathrm{gem}} = -13.27 \pm 0.044$ Hz.)

Anal. Calcd for $C_9H_{10}OS_2$: C, 54.51; H, 5.08; S, 32.34. Found: C, 55.05; H, 5.10; S, 31.94.

Reaction of 3-Methylthieno[3,2-*b*]thiophen-2(5*H*)-one (9b) with Diazoethane. A solution of **9b** (3.3 g) and diazoethane (2 g) in ether was stirred at room temperature for 9 hr and then worked up as described above for compound **9a.** The two identified products were **10** and **11;** other compounds were formed in minute amounts and their identification was not possible.

2-Ethoxy-3-ethylazothieno[3,2-*b*]thiophene (5). A solution of thieno[3,2-*b*]thiophene-2,3-dione 3-ethylhydrazone (**3**, 1 g) in ether was treated with excess diazoethane and stirred at room temperature for 2 hr. The solvent was evaporated and the residue was chromatographed through silica gel using light petroleum–ether (9:1) as eluent. The product obtained (0.9 g) was purified by distillation: bp 137° (0.5 mm); NMR (CS_2) δ_5 7.10, δ_6 6.90, $\delta_{\mathrm{OCH_2CH_3}}$ 4.46, $\delta_{\mathrm{NCH_2CH_3}}$ 3.98, $\delta_{\mathrm{OCH_2CH_3}}$ 1.48, $\delta_{\mathrm{NCH_2CH_3}}$ 1.39, $J_{5-6} = 5.25$, $J_{\mathrm{OCH_2CH_3}} = 7.0$, $J_{\mathrm{NCH_2CH_3}} = 7.5$ Hz.

Anal. Calcd for $C_{10}H_{12}N_2OS_2$: C, 49.97; H, 5.03; N, 11.66; S, 26.68. Found: C, 50.40; H, 5.03; N, 11.66; S, 26.48.

2-Ethoxy-3-methylazothieno[3,2-*b*]thiophene (8). A solution of thieno[3,2-*b*]thiophene-2,3-dione 3-methylhydrazone (**7**, 0.3 g) was treated with excess diazoethane and the reaction mixture worked up as described above for **5**. The azo compound was obtained as an oil, which was purified by distillation: bp 125° (0.5 mm); NMR (CS_2) δ_5 7.15, δ_6 6.95, $\delta_{\mathrm{CH_2CH_3}}$ 4.5, $\delta_{\mathrm{CH_2CH_3}}$ 1.5, $\delta_{\mathrm{NCH_3}}$ 3.93, $J_{5-6} = 5.25$, $J_{\mathrm{CH_2CH_3}} = 7.0$ Hz.

Anal. Calcd for $C_9H_{10}N_2OS_2$: C, 47.76; H, 4.45; N, 12.38; S, 28.33. Found: C, 47.90; H, 4.25; N, 12.50; S, 28.10.

3-Benzylidenethieno[3,2-*b*]thiophen-2-one (18). A stirred solution of thieno[3,2-*b*]thiophen-2(3*H*)-one (**1a**, 0.6 g) and benzaldehyde (0.4 g) in ethanol (10 ml), cooled in an ice bath, was treated with gaseous HCl. A yellow product precipitated after a few minutes and stirring was continued for 30 min. The solid was filtered off and crystallized from ethanol to give 0.7 g of **18:** mp 107–108°; NMR (CS_2) δ_5 7.24, δ_6 6.93, $\delta_{=\mathrm{CH}}$ 7.30, $\delta_{\mathrm{C_6H_5}}$ 7.32–7.75, $J_{5-6} = 5.25$, $J_{=\mathrm{CH}\text{-}5} = 0.7$ Hz; ir (CCl_4) 1700 cm^{-1} (C═O).

Anal. Calcd for $C_{13}H_8OS_2$: C, 63, 91; H, 3.30; S, 26.24. Found: C, 64.09; H, 3.28; S, 26.07.

3-Acetonylidene-5-methylthieno[3,2-*b*]thiophen-2-one (19). This compound was obtained as a yellow solid melting at 118–119°, after crystallization from ethanol, when 5-methylthieno[3,2-*b*]thiophen-2(3*H*)-one[2] was chromatographed through an alumina column and a mixture (3:1) of light petroleum and acetone was used as eluent: NMR (CS_2) δ_6 6.52, δ_5 2.57, $\delta_{\mathrm{CH_3\text{-}1}}$ 2.23, $\delta_{\mathrm{CH_3\text{-}2}}$ 2.40, $J_{5-6} = 1.1$ Hz; ir (CCl_4) 1690 cm^{-1} (C═O).

Anal. Calcd for $C_{10}H_{10}OS_2$: C, 57.11; H, 4.79; S, 30.49. Found: C, 57.09; H, 4.80; S, 30.36.

3-Acetonyliden-6-*tert*-butylthieno[3,2-*b*]thiophen-2-one (20). This product was obtained from 6-*tert*-butylthieno[3,2-*b*]thiophen-2(3*H*)-one[2] following the procedure described above for **19:** mp 83–85° from ethanol; NMR (CS_2) δ_5 6.87, δ_6 1.3, $\delta_{\mathrm{CH_3\text{-}1}}$ 2.22, $\delta_{\mathrm{CH_3\text{-}2}}$ 2.38; ir (CCl_4) 1690 cm^{-1} (C═O).

Anal. Calcd for $C_{13}H_{16}OS_2$: C, 61.86; H, 6.39; S, 25.41. Found: C, 61.16; H, 6.53; S, 25.75.

5-Benzylidene-3-methylthieno[3,2-*b*]thiophen-2-one (21). This compound was prepared from **9b** or **9a** following the procedure reported above for **18:** mp 128–129° from ethanol; NMR (CS_2) $\delta_{\mathrm{C_6H_5}}$ 7.1–7.6, δ_6 6.72, $\delta_{=\mathrm{CH}-}$ 6.92, $\delta_{\mathrm{CH_3}}$ 1.96; ir (CCl_4) 1685 cm^{-1} (C═O).

Anal. Calcd for $C_{14}H_{10}OS_2$: C, 65.08; H, 3.90; S, 24.82. Found: C, 65.17; H, 3.80; S, 24.69.

5-Benzylidene-3,6-dimethylthieno[3,2-*b*]thiophen-2-one (22). This compound was obtained from 3,6-dimethylthieno[3,2-*b*]thiophen-2(5*H*)-one[2] according to the procedure reported above for **18:** mp 196–197° from ethanol; NMR (CS_2) $\delta_{\mathrm{C_6H_5}}$ 7.2–7.7, $\delta_{=\mathrm{CH}-}$ 7.0, δ_5 2.31, δ_3 2.03; ir (CCl_4) 1690 cm^{-1} (C═O).

Anal. Calcd for $C_{15}H_{12}OS_2$: C, 66.14; H, 4.44; S, 23.54. Found: C, 65.94; H, 4.60; S, 23.58.

2-Benzoyloxythieno[3,2-*b*]thiophene (23). A solution of thieno[3,2-*b*]thiophen-2(3*H*)-one (**1a**, 0.16 g) in 10% NaOH (1.5 ml) was treated with benzoyl chloride (0.15 g). A precipitate was formed which was extracted with ether. Evaporation of the solvent left a solid compound which was purified by crystallization from ethanol: mp 113–114°; NMR (CS_2) δ 8.18–8.01 (2 H, ortho protons), 7.6–7.35 (3 H, meta and para protons), δ_3 6.99, δ_6 7.08, δ_5 7.20, $J_{5-6} = 5.2$, $J_{3-6} = 0.7$ Hz; ir (CCl_4) 1760–1740 cm^{-1} (C═O).

Anal. Calcd for $C_{13}H_8O_2S_2$: C, 59.98; H, 3.10; S, 24.63. Found: C, 58.80; H, 3.13; S, 24.30.

2-Benzoyloxy-3-methylthieno[3,2-*b*]thiophene (24). This compound was prepared in 55% yield from either **9b** or **9a,** according to the procedure reported above for **23:** mp 89–90° from ethanol; NMR (CS_2) δ 8.20–8.03 (2 H, ortho protons), 7.6–7.3 (3 H, meta and para protons), δ_6 7.08, δ_5 7.18, $\delta_{\mathrm{CH_3}}$ 2.28, $J_{5-6} = 5.2$ Hz; ir (CCl_4) 1760–1740 cm^{-1} (C═O).

Anal. Calcd for $C_{14}H_{10}O_2S_2$: C, 61.29; H, 3.67; S, 23.37. Found: C, 61.30; H, 3.53; S, 23.28.

2-Benzoyloxy-5-methylthieno[3,2-*b*]thiophene (25). This compound was obtained in 45% yield from 5-methylthieno[3,2-*b*]thiophen-2(3*H*)-one[2] after treatment with benzoyl chloride as described above for **23:** mp 130–131° from ethanol; NMR (CS_2) δ 8.2–8.0 (2 H, ortho protons), 7.6–7.3 (3 H, meta and para protons), δ_3 6.88, δ_6 6.73, $\delta_{\mathrm{CH_3}}$ 2.55, $J_{3-6} = 0.6$, $J_{6\text{-}\mathrm{CH_3}} = 1.2$ Hz; ir (CCl_4) 1760–1740 cm^{-1} (C═O).

Anal. Calcd for $C_{14}H_{10}O_2S_2$: C, 61.29; H, 3.67; S, 23.37. Found: C, 61.20; H, 3.79; S, 23.51.

2-Benzoyloxythieno[2,3-*b*]thiophene (26). This compound was obtained in 60% yield from thieno[2,3-*b*]thiophen-2(3*H*)-one[2] after treatment with benzoyl chloride as described above for **23:** mp 109–110° from ethanol; NMR (CS_2) δ 8.18–8.0 (2 H, ortho protons), 7.6–7.35 (3 H, meta and para protons), δ_3 6.95, δ_4 7.09, δ_5 7.23, $J_{4-5} = 5.2$ Hz; ir (CCl_4) 1760–1740 cm^{-1} (C═O).

Anal. Calcd for $C_{13}H_8O_2S_2$: C, 59.98, H, 3.10; S, 24.63. Found: C, 59.10; H, 3.15; S, 24.95.

2-Benzoyloxy-3-methylthieno[2,3-*b*]thiophene (27). The product was prepared in 52% yield from 3-methylthieno[2,3-*b*]thiophen-2(3*H*)-one[2] according to the procedure reported above for **23:** mp 95–96° from ethanol; NMR (CS_2) δ 8.18–8.0 (2 H, ortho protons), 7.6–7.3 (3 H, meta and para protons), δ_5 7.20, δ_4 7.02, $\delta_{\mathrm{CH_3}}$ 2.29, $J_{4-5} = 5.2$ Hz; ir (CCl_4) 1760–1740 cm^{-1} (C═O).

Anal. Calcd for $C_{14}H_{10}O_2S_2$: C, 61.29; H, 3.67; S, 23.37. Found: C, 61.27; H, 3.81; S, 23.29.

2-Benzoyloxy-5-methylthieno[2,3-*b*]thiophene (28). This product was obtained in 50% yield from 5-methylthieno[2,3-*b*]thiophen-2(3*H*)-one[2] according to the procedure reported above for **23:** mp 146–148° from ethanol; NMR (CS_2) δ 8.18–8.0 (2 H, ortho protons), 7.6–7.3 (3 H, meta and para protons), δ_3 6.68, δ_4 6.74, $\delta_{\mathrm{CH_3}}$ 2.55, $J_{\mathrm{CH_3\text{-}4}} = 1.1$ Hz; ir (CCl_4) 1760–1740 cm^{-1} (C═O).

Anal. Calcd for $C_{14}H_{10}O_2S_2$: C, 61.29; H, 3.67; S, 23.37. Found: C, 60.59; H, 3.97; S, 23.85.

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Registry No.—**1a**, 56411-71-3; **2**, 56412-20-5; **3**, 56412-21-6; **4**, 56412-22-7; **5**, 56412-23-8; **6**, 56412-24-9; **7**, 56412-25-0; **8**, 56412-26-1; **9a**, 56411-72-4; **9b**, 56411-73-5; **10**, 56412-27-2; **11**, 56412-28-3; **18**, 56412-29-4; **19**, 56412-30-9; **20**, 56412-31-8; **21**, 56412-32-9; **22**, 56412-33-0; **23**, 56412-34-1; **24**, 56412-35-2; **25**, 56412-36-3; **26**, 56412-37-4; **27**, 56412-38-5; **28**, 56412-39-6; 2-bromothieno[3,2-*b*]thiophene, 25121-82-8; sodium methoxide, 124-41-4; sodium ethoxide, 141-52-6; 2-bromo-3-methylthieno[3,2-*b*]thiophene, 56411-95-1; diazoethane, 1117-96-0; diazomethane, 334-88-3; benzaldehyde, 100-52-7; 5-methylthieno[3,2-*b*]thiophen-2(3*H*)-one, 56411-78-0; 6-*tert*-butylthieno[3,2-*b*]thiophen-2(3*H*)-one, 56411-80-4; 3,6-dimethylthieno[3,2-*b*]thiophen-2(5*H*)-one, 56411-85-9; benzoyl chloride, 98-88-4; thieno[2,3-*b*]thiophen-2(3*H*)-one, 56411-86-0; 3-methylthieno[2,3-*b*]thiophen-2(3*H*)-one, 56411-87-1; 5-methylthieno[2,3-*b*]thiophen-2(3*H*)-one, 56411-91-7.

References and Notes

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