Preparation and Tautomeric Structures of Some Potential 2,5-Dihydroxythieno[3,2-*b*]thiophenes

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Some potential alkyl- and aryl-substituted 2,5-dihydroxythieno[3,2-*b*]thiophenes have been prepared and their structures determined by NMR spectroscopy. In no case could evidence be found for the presence of the hydroxy forms of these compounds which instead exist as dithiolactones. The preferred structure is in every case that of thieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-diones (b). Only in the unsubstituted compound could the thieno[3,2-*b*]thiophen-2,5(3*H*,6*H*)-dione form (a) be obtained; this, however, rapidly transforms into b. In the case of the 6-substituted compounds, two stereoisomers of form b were obtained having opposite configuration at C-6. The effect of the nature and the position of substituents on the stability of the tautomeric forms is examined and discussed.

In recent papers we described the synthesis, the tautomeric properties,[1] and the chemical behavior[2] of several alkyl- and aryl-substituted potential 2-hydroxythieno[3,2-*b*]thiophenes and 2-hydroxythieno[2,3-*b*]thiophenes. It was found that these compounds do not exist in the hydroxy form but have the structures of thiolactones. In the case of the thieno[2,3-*b*]thiophen system all of the compounds examined have the structure of thieno[2,3-*b*]thiophen-2(3*H*)-ones, while in the case of the [3,2-*b*] system a tautomeric equilibrium exists between the thieno[3,2-*b*]thiophen-2(3*H*)-ones and the thieno[3,2-*b*]thiophen-2(5*H*)-ones. The effects of the nature and the position of the substituents on the tautomeric equilibria have been explored.[1]

We report now the result of an investigation carried out on the potential 2,5-dihydroxythieno[3,2-*b*]thiophenes, **1–6**,[3] which present interesting tautomeric properties; these compounds also represented the starting materials for the synthesis of the corresponding thieno[3,2-*b*]thiophen-2,5-diones (**8**) which have been used as very suitable models for an ESR investigation of the intramolecular cation exchange in paramagnetic ion pairs.[4]

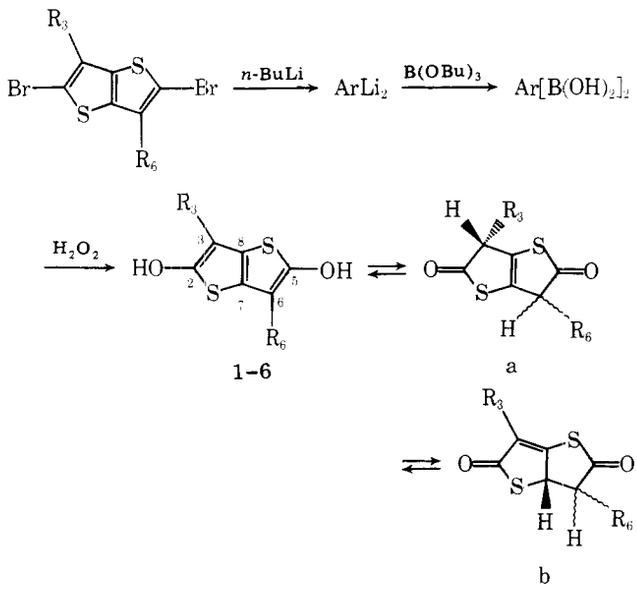
The products described in this paper were obtained through the hydrogen peroxide oxidation of the diboronic acids of thienothiophenes, as indicated in Scheme I. This synthetic method was introduced for the preparation of hydroxythiophenes[5] and also employed in the case of the monohydroxythienothiophenes[1] with very good results.

For these compounds, besides the hydroxy form, two other tautomeric structures can be written, the thieno[3,2-*b*]thiophen-2,5(3*H*,6*H*)-diones (a) and the thieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-diones (b). Moreover, depending on the nature of the substituents R_3 and R_6, other stereoisomers are possible for tautomers a and b according to the configuration of C-6. The structures of the possible isomers can be confidently assigned by NMR spectroscopy.

In no case was evidence obtained for the existence of the hydroxy forms, all the compounds investigated being a mixture of the dithiolactones a and/or b. Compounds **1–6** were always accompanied by small amounts of the monohydroxy derivatives,[1] in the tautomeric forms **7a** or/and **7b**, whose formation was very probably due to incomplete transformation of the dilithium compounds into the boronic acids. A second by-product was the thieno[3,2-*b*]thiophen-2,5-dione (**8**), which very easily forms[4] through the oxidation of **1–6** (Scheme II).

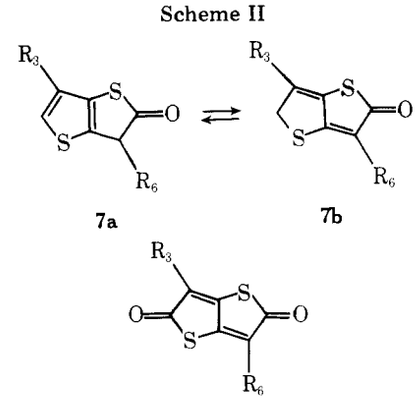
From the oxidation of the 2,5-thieno[3,2-*b*]thienyl diboronic

Scheme I



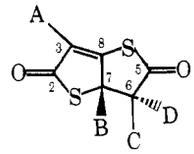
1, $R_3 = R_6 = H$ 4, $R_3 = CMe_3$; $R_6 = H$
2, $R_3 = R_6 = Me$ 5, $R_3 = Me$; $R_6 = H$
3, $R_3 = R_6 = Ph$ 6, $R_3 = Ph$; $R_6 = H$

Scheme II



0022-3263/78/1943-2197$01.00/0

Table I.[a] **Physical and NMR (in CS_2) Data of the Thieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-diones**



Compound	Mp, °C	Chemical shifts				Coupling constants, Hz				
		A	B	C	D	J_{AB}	J_{BC}	J_{BD}	J_{CD}	J_{AC}
1b (R_3 = R_6 = H)	115–116	6.25	4.88	3.28	2.75	2.1	7.8	12	16.2	0.8
2b (R_3 = R_6 = Me)	130–132	1.9[b]	4.38	1.41[b]	2.7	2.0[f]		12	6.7[c]	
2b' (R_3 = R_6 = Me)	*d*	1.9[b]	4.82	3.1	1.1[b]	2.0[f]	7.2		7.5[c]	
4b (R_3 = CMe_3; R_6 = H)	108–110	1.3[e]	4.67	3.21	2.73		7.5	12.3	15.9	
4b' (R_3 = H; R_6 = CMe_3)	*d*	6.22	4.82	1.11[e]	2.78	2.1		11.1		
5b (R_3 = Me; R_6 = H)	110–111	1.9[b]	4.72	3.25	2.66	2.0[f]	7.8	11.8	15.9	
6b (R_3 = Ph; R_6 = H)	145–147	7.35[g]	4.82	3.24	2.69		7.7	12	16.2	

[a] Satisfactory analytical data were reported for all the compounds listed in the table. [b] Methyl group. [c] $J_{H_6\text{-}CH_3}$. [d] Not isolated (the NMR data were obtained from the spectrum of the mixture with the b isomer). [e] *tert*-Butyl group. [f] $J_{CH_3\text{-}H_7}$. [g] Phenyl group.

acid a single crystalline product was obtained in good yields, whose NMR spectrum was constituted by a singlet at δ 3.62; this compound presented the characteristic carbonyl stretching vibration in the infrared spectrum. On the basis of these spectroscopic results and of its analytical data, the structure of thieno[3,2-*b*]thiophen-2,5(3*H*,6*H*)-dione (**1a**) has been assigned to this compound. Product **1a,** however, is not very stable and on standing or on attempted column chromatography is completely and irreversibly transformed into a new crystalline compound, which in the light of its NMR spectrum was assigned the structure of the thieno[3,2-*b*]-thiophene-2,5(6*H*,7*H*)-dione (**1b**) (Scheme III). Treatment of a solution of **1a** with HCl gas results in instantaneous transformation into **1b.**

The NMR data of **1b** are reported in Scheme III; the portion of the spectrum due to the protons H_B, H_C, and H_D was analyzed as an ABX system, with coupling with H_A considered as first-order perturbations, which was justified by the $\Delta\delta/J$ ratios involved. Assignment of H_A and H_B can be confidently made on the basis of their chemical shifts and also in the light of the spectra of substituted products which will be discussed later (see Table I). Difficulties are instead encountered in the relative assignment of the two geminal protons H_C and H_D. The assignments indicated in Scheme III are based on the values of the vicinal coupling constants, J_{BC} and J_{BD}, under the assumption that the Karplus equation also holds for the systems under investigation. Thus, the larger J_{vic} (12 Hz) is assigned to the protons H_B and H_D which, as can be seen in the Newman projection along the C_6–C_7 bond reported in Scheme III, are in anti, and the smaller J_{vic} (7.8 Hz) to the protons H_B and H_C which are in a gauche position. This assignment is also confirmed by the long-range coupling (0.8 Hz) observed between H_A and one of the two geminal protons; this proton is H_C, because, as showed by molecular models, H_A and H_C are separated by an almost planar zig-zag pathway, while the C_6–H_D bond lies almost perpendicular to that plane. These assignments are of particular interest because they allow stereochemical assignments in the substituted compounds.

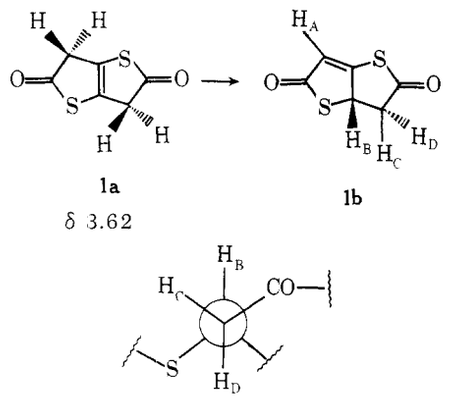
The easy isomerization of **1a** to **1b** is understandable in view of the greater thermodynamic stability of the latter compound where the carbonyl group is conjugated with the carbon–carbon double bond.

The reaction mixture of **2** showed the presence of two isomers in almost equimolecular amounts. Their NMR data are collected in Table I and clearly indicate that in this case we are dealing with two isomeric 3,6-dimethylthieno[3,2-*b*]-thiophen-2,5(6*H*,7*H*)-diones, which differ in the configuration at C-6. With respect to proton H_B, the hydrogen atom in C-6 in one case, **2b** (H_D), is anti and in the other, **2b'** (H_C), is gauche (Scheme IV).

On the basis of the assignments reported above for the parent compound, the isomer presenting the larger J_{vic} was assigned the structure **2b.** This tautomer is also the thermodynamically more stable, since on treating the mixture of the two isomers with acids, or on standing, an equilibrium composition was reached in which the **2b/2b'** ratio has the value of 85:15. Pure **2b** could be obtained by crystallization and, after treatment with HCl gas, the same equilibrium mixture of **2b** and **2b'** was obtained.

An X-ray crystal structure determination of **2b** has been carried out[6] and this demonstrated that the two hydrogens

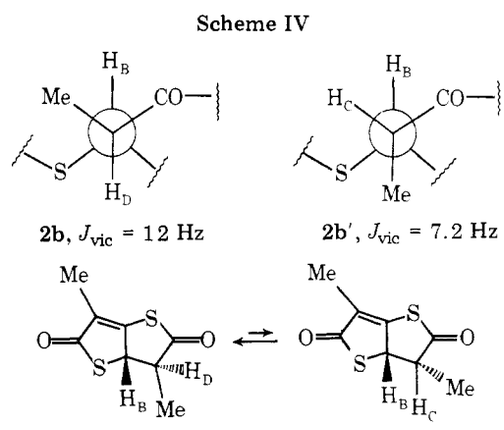
Scheme III



1a δ 3.62 → **1b**

δ_A 6.25; δ_B 4.88; δ_C 3.28; δ_D 2.75
J_{AB} = 2.1; J_{AC} = 0.8; J_{BC} = 7.8; J_{BD} = 12; J_{CD} = 16.2 Hz

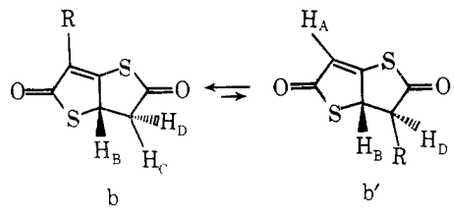
Scheme IV



2b, J_{vic} = 12 Hz **2b'**, J_{vic} = 7.2 Hz

Equilibrium composition: 2b/2b' = 85:15

Scheme V



b b′

4, R = CMe_3
5, R = Me
6, R = Ph

bonded at C-6 and C-7 are in the anti position, the torsional angle H_6–C_6–C_7–H_7 being 174°. This result unambiguously confirms the proposed structures and at the same time demonstrates the exact interpretation of the NMR spectra of **1b** and of the other compounds described below.

From the reaction of the diphenyl derivative (**3**), the desired products were not formed at all, the only compound obtained being the 3,6-diphenylthieno[3,2-*b*]thiophen-2,5-dione (**8**) (R_3 = R_6 = Ph). In the case of the 3-methyl-(**5**) and 3-phenyl-(**6**) derivatives only the isomers b were observed (Scheme V).

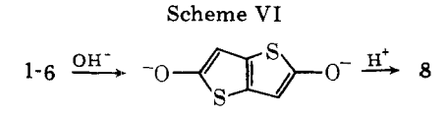
This is not unexpected since in these isomers the substituents can hyperconjugate or conjugate with the double bond thus achieving maximum stability. In fact when the substituent is a *tert*-butyl group, compound (**4**), a mixture of two isomeric 2,5(6*H*,7*H*)-diones in almost equimolecular amounts was obtained. The NMR of one of the two tautomers presented the usual ABX system leaving no doubts that it possesses the **4b** structure. The NMR spectrum of the other isomers (see Table I) clearly indicated that the *tert*-butyl group is bonded to C-6. Moreover, long-range coupling between H_A and the proton in C-6 was not observed and the J_{vic} has the value of 11.3 Hz. These observations indicate that the two vicinal protons are anti as indicated in structure **4b′** in Scheme V. The other possible stereoisomer with the two vicinal protons in gauche was not observed. Equilibration of the mixture of the two isomers gave a **4b**/**4b′** ratio of 90:10.

All of the results described above indicate that the preferred tautomeric form of these potential dihydroxythienothiophenes is in every case that of the thieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (b). Whenever a substituent is present which can conjugate or hyperconjugate with the carbon–carbon double bond this is the only form which is obtained; the thieno[3,2-*b*]thiophen-2,5(3*H*,6*H*)-dione (a) is in fact observed only in the case of the unsubstituted compound (**1**).

Moreover, substituents bonded at C-6 of the 2,5(6*H*,7*H*)-diones (b) preferentially assume a gauche position with respect to the bridgehead proton, H_B. This isomer is dominant in the case of a methyl group (compound **2b**) and becomes the only one present in the case of the *tert*-butyl group (compound **4b′**), clearly indicating that the observed difference in stability is governed by steric effects.

In the case of hydroxythiophenes,[7] 2-hydroxythieno[3,2-*b*]thiophenes,[1] and 2,5-dihydroxythieno[2,3-*b*]thiophenes,[8] the base extraction method can be used to regenerate the thermodynamically less stable tautomeric forms. Application of this procedure to the products of the present investigation failed to give the expected results; in every case acidification of the alkaline solution of **1–6** afforded only the oxidation products, thieno[3,2-*b*]thiophenes-2,5-diones (**8**) (Scheme VI). This method was utilized for the synthesis of the dithiolactones **8** necessary for an ESR investigation of their radical anions.[4]

Scheme VI



Experimental Section[9]

(A). Thieno[3,2-*b*]thiophenes. With the exception of the 3-*tert*-butyl derivative, all the other thieno[3,2-*b*]thiophenes necessary for the present work were already described in the literature.

3-*tert*-Butylthieno[3,2-*b*]thiophene (9). A solution of 3-mercaptothiophene[10] in methanol (40 mL) containing sodium methoxide (from 2.3 g of Na) was added dropwise, at 0 °C, to a solution of bromopinacolone[11] (20 g) in methanol (60 mL) and the mixture was stirred overnight at room temperature. The solvent was evaporated and the residue dissolved in water and ether. The organic layer was washed, dried, and evaporated and the residue distilled to afford 3-thienylthiopinacolone (18 g), bp 130 °C (2 mm): NMR (CS_2) δ_{CMe_3} 1.1, δ_{CH_2} 3.7, δ_{Ar} 6.8–7.2.

Anal. Calcd for $C_{10}H_{14}OS_2$: C, 56.03; H, 6.6. Found: C, 55.95; H, 6.57. The ketone (7.5 g) in CS_2 (40 mL) was added dropwise to a stirred suspension of $AlCl_3$ (5.8 g) in CS_2 (80 mL) and stirring was continued for 22 h. The mixture was poured onto ice and hydrochloric acid and extracted with ether. The organic layer was washed, dried, and evaporated; the residue was distilled under vacuum to afford 3.2 g of **9**: bp 113 °C (2 mm); NMR (CS_2) δ_{CMe_3} 1.35, δ_2 6.84, δ_5 7.17, δ_6 7.03, J_{5-6} = 5.25 Hz, J_{2-5} = 1.5 Hz.

Anal. Calcd for $C_{10}H_{12}S_2$: C, 61.17: H, 6.17. Found: C, 61.37; H, 6.20.

(B). 2,5-Dibromothieno[3,2-*b*]thiophenes. These compounds were prepared from the thieno[3,2-*b*]thiophenes according to the following general procedure. To a solution of the thieno[3,2-*b*]thiophene (0.01 mol) in acetic acid (150 mL) *N*-bromosuccinimmide (0.02 mol) was added in small portions and the mixture was stirred for 2 h. The solution was poured onto water and extracted with chloroform several times; the organic layer was separated, washed with water and $NaHCO_3$ solution, and dried. The solvent was evaporated and the residue crystallized from ethanol or distilled under vacuum.

2,5-Dibromothieno[3,2-*b*]thiophene (10). Mp 128–129 °C (lit.[12] 129.5–131 °C).

2,5-Dibromo-3,6-dimethylthieno[3,2-*b*]thiophene (11). Yields 89%; mp 140–142 °C (lit.[1] 140–142 °C).

2,5-Dibromo-3,6-diphenylthieno[3,2-*b*]thiophene (12). Yields 90%; mp 252–254 °C; NMR (CS_2) $\delta_{C_6H_5}$ 7.38.

Anal. Calcd for $C_{18}H_{10}Br_2S_2$: C, 48.02; H, 2.24; Br, 35.50; S, 14.24. Found: C, 48.03; H, 2.26; Br, 35.37; S, 14.26.

2,5-Dibromo-3-*tert*-butylthieno[3,2-*b*]thiophene (13). Yields 92%; bp 150 °C (1 mm); NMR (CS_2) δ_{CMe_3} 1.52, δ_6 6.92.

Anal. Calcd for $C_{10}H_{10}Br_2S_2$: C, 33.9; H, 2.85. Found: C, 34.02; H, 2.90.

2,5-Dibromo-3-methylthieno[3,2-*b*]thiophene (14). Yields 85%; mp 74–75 °C; NMR (CS_2) δ_{CH_3} 2.25, δ_6 7.08.

Anal. Calcd for $C_7H_4Br_2S_2$: C, 26.94; H, 1.29. Found: C, 26.98; H, 1.28.

2,5-Dibromo-3-phenylthieno[3,2-*b*]thiophene (15). Yields 92%; mp 118–120 °C; NMR (CS_2) δ_6 7.0, $\delta_{C_6H_5}$ 7.38.

Anal. Calcd for $C_{12}H_6Br_2S_2$: C, 38.52; H, 1.62. Found: C, 38.38; H, 1.63.

(C). Synthesis of Potential 2,5-Dihydroxythieno[3,2-*b*]thiophenes (1–6). The syntheses of these compounds have been carried out according to the general procedure described below for the parent compound (**1**). Details on the workup of the reaction mixtures are also reported for the single products, whose physical and spectral data are collected in Table I.

Thieno[3,2-*b*]thiophen-2,5(3*H*,6*H*)-dione (1a) and Thieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (1b). To a stirred solution of *n*-butyllithium (prepared from 0.42 g of Li) in ether, cooled at −60 °C, an ethereal solution of 2,5-dibromothieno[3,2-*b*]thiophene (**10**) (3 g) was added dropwise. The resulting solution was stirred for 30 min at −30 °C and then treated, at −70 °C, with *n*-butyl borate (10 g) in ether. The mixture was left to gradually reach room temperature during 5 h and then shaken with 2 N HCl (25 mL). The layers were separated and the aqueous phase extracted with ether. The ethereal solution was extracted with three portions of 100 mL of cold 2 N NaOH and the alkaline solution was acidified with cold 2 N H_2SO_4; the separating diboronic acid was dissolved in ether and 35% hydrogen peroxide (20 mL) was added. The mixture was vigorously stirred, under nitrogen, for 15 h. The ethereal solution was washed several times with water and dried over Na_2SO_4, and the solvent was evaporated under nitrogen. The residue was washed with pentane.

An NMR spectrum of the solid residue (1.3 g) showed the presence of **1a** and small amounts of **8** (R_3 = R_6 = H); bubbling HCl gas into

the solution caused the rapid and complete transformation of **1a** into **1b**.

A portion of the solid residue was washed with cold carbon disulfide, which left undissolved the pure thieno[3,2-*b*]thiophen-2,5(3*H*,6*H*)-dione (**1a**), mp 104–105 °C; NMR (CS_2) δ 3.62.

Anal. Calcd for $C_6H_4O_2S_2$: C, 41.84; H, 2.35; S, 37.23. Found: C, 41.58; H, 2.34; S, 37.5. The remaining part of the solid residue and the part dissolved in CS_2 were chromatographed through a silica gel column using light petroleum ether (9:1) as eluent. The first fractions contained the yellow thieno[3,2-*b*]thiophen-2,5-dione[4] (**8**) (0.1 g), mp 155–156 °C. Fractions were then collected which contained the thieno[3,2-*b*]thiophen-2,5(6*H*, 7*H*)-dione (**1b**).

3,6-Dimethylthieno[3,2-*b*]thiophen-2,5(6*H*, 7*H*)-diones (2b and 2b'). The NMR spectrum of the crude residue (3.6 g) obtained from the reaction of **11** (7.5 g) showed the presence of compounds **2b** and **2b'** in the ratio of 60:40, together with lower amounts of **7a** (R_3 = R_6 = Me) and **8** (R_3 = R_6 = Me). The components were separated by column chromatography as described above for the reaction of **1**. The first fractions contained the yellow dione **8**[4] (0.2 g), mp 151–152 °C. Further elution afforded a mixture of the two isomers **2b** and **2b'** (2.5 g); crystallization from acetone–pentane gave pure **2b**, mp 130–132 °C. The solution of this compound, as well as those containing the two isomers in different proportions, when treated with HCl gas, gave a mixture of **2b** and **2b'** in the ratio of 85:15. Finally, fractions were collected containing compound **7b**[1] (0.5 g), mp 125–127 °C.

3,6-Diphenylthieno[3,2-*b*]thiophen-2,5-dione (8) (R_3 = R_6 = Ph). The reaction carried out on **12** (2.7 g) afforded as the sole product the dione **8** (1.3 g), mp 224–225 °C.[4,13]

3-Methylthieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (5b). Reaction of **14** (5.5 g) afforded a solid residue (2.8 g) which was chromatographed to give the following fractions: (i) compound **8** (R_3 = Me; R_6 = H) (0.1 g), mp 91–93 °C,[4] (ii) compound **7a** (R_3 = Me; R_6 = H)[1] (0.7 g) which on standing gradually transforms in a mixture of **7a** and **7b**,[1] and (iii) compound **5b** (1.4 g), mp 109–110 °C from ethanol.

3-Phenylthieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (6b). The reaction carried out on 7.5 g of **15** afforded 3.7 g of residue which was worked up in the usual way to give (i) the dione **8** (R_3 = Ph; R_6 = H) (0.1 g), mp 124–126 °C,[1] (ii) compound **7a** (R_3 = Ph; R_6 = H)[1] (0.4 g), and (iii) the product **6b** (2.8 g), mp 145–147 °C from ethanol.

3-*tert*-Butylthieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (4b) and 6-*tert*-Butylthieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (4b'). The reaction was carried out on 5 g of **13**. The solid residue (3.2 g) was constituted by **8** (R_3 = CMe_3; R_6 = H), **7a** (R_3 = CMe_3; R_6 = H) and an equimolecular mixture of **4b** and **4b'**. The various components were separated by column chromatography in the usual way. The first fractions contained the dione **8**, mp 133–135 °C[4] (0.2 g); then 3-*tert*-butylthieno[3,2-*b*]thiophen-2(3*H*)-one, **7a** (0.7 g), mp 53–55 °C,[1] was collected. The following fractions contained mixtures, in different proportions, of **4b** and **4b'**; evaporation of the solvent left 2 g of residue. The mixture was crystallized from ethanol to afford pure 3-*tert*-butylthieno[3,2-*b*]thiophen-2,5(6*H*,7*H*)-dione (**4b**), mp 108–110 °C (1.6 g). This compound, as well as the mixtures with the isomeric **4b'**, when treated with HCl gas, gave a mixture of **4b** and **4b'** in the ratio of 90:10.

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Registry No.—**1a**, 65701-76-0; **1b**, 65701-77-1; **2b**, 61414-32-2; **2b'**, 65701-78-2; **4b**, 65701-79-3; **4b'**, 65701-80-6; **5b**, 65701-81-7; **6b**, 65701-82-8; **7a** (R_3 = R_6 = Me), 56411-84-8; **7a** (R_3 = Me; R_6 = H), 56411-82-6; **7a** (R_3 = Ph; R_6 = H), 56411-81-5; **7a** (R_3 = CMe_3; R_6 = H), 56411-80-4; **7b** (R_3 = R_6 = Me), 56411-85-9; **7b** (R_3 = Me; R_6 = H), 56411-83-7; **8** (R_3 = R_6 = H), 60749-71-5; **8** (R_3 = R_6 = Me), 60749-72-6; **8** (R_3 = R_6 = Ph), 51752-01-3; **8** (R_3 = Me; R_6 = H), 60749-73-7; **8** (R_3 = Ph; R_6 = H), 60749-76-0; **8** (R_3 = CMe_3; R_6 = H), 60749-75-9; **9**, 65701-83-9; **10**, 25121-87-3; **11**, 56412-13-6; **12**, 65701-84-0; **13**, 65701-85-1; **14**, 65701-86-2; **15**, 65701-87-3; 3-mercaptothiophene, 7774-73-4; bromopinacolone, 5469-26-1; 3-thienylthiopinacolone, 65701-88-4; thieno[3,2-*b*]thiophene, 251-41-2; 3,6-dimethylthieno[3,2-*b*]thiophene, 56412-11-4; 3,6-diphenylthieno[3,2-*b*]thiophene, 21210-92-4; 3-methylthieno[3,2-*b*]thiophene, 1723-34-8; 3-phenylthieno[3,2-*b*]thiophene, 35022-15-2.

References and Notes

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Acid-Catalyzed Reaction of 1,6-Dioxaspiro[4.4]nonane with Ferrocene

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1,6-Dioxaspiro[4.4]nonane reacts with ferrocene in the presence of aluminum chloride or boron trifluoride etherate to give 2-ferrocenyl-2-(3-hydroxypropyl)tetrahydrofuran (**5**). Treatment of **5** with methyl Grignard gives 4-methyl-4-ferrocenylheptane-1,7-diol (**7**). Reaction of **5** with trifluoroacetic acid gives ferrocenylbis(3-trifluoroacetoxypropyl)carbonium trifluoroacetate (**8a**). Treatment of **8a** with aqueous base gives 4-ferrocenyl-3-heptene-1,7-diol (**6**). With trifluoroacetic acid as catalyst, 1,6-dioxaspiro[4.4]nonane reacts with ferrocene to give a mixture of **5**, **6**, 4,4-diferrocenylheptane-1,7-diol (**3**), and 1,1'-bis[4-(4-ferrocenyl-1,7-dihydroxy)heptyl]ferrocene (**9**). Ferrocene and the ferrocene derivatives exist in an equilibrium condition in this reaction.

A few diferrocenylmethane derivatives with alkyl or substituted alkyl groups attached to the quaternary carbon have been reported.[1,2] They are made by the acid-catalyzed reaction of ketones with ferrocene. Compound **2**, R' = CH_2CH_2OH, and derivatives of **2**, R' = $CH_2CO_2CH_3$, have been used to chemically attach ferrocene derivatives onto specially designed polyurethane systems.[3] One objective of the present work was to prepare 4,4-diferrocenylheptane-1,7-diol (**3**) as a constit-