The Synthesis of Thiophenium and of Oxazolium Salts from Diazoketones

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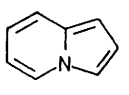
4-Diazoacetylthianthren with perchloric acid in acetonitrile gave 2-oxo-1,2-dihydrothieno[3,2,1-*de*]-thianthrenium perchlorate which gave the corresponding enol ether with diazomethane. This ether was compared with 3-methoxy-1-methylbenzo[*b*]thiophenium perchlorate, prepared from 3-methoxythiophen, and which was much more stable to solvolysis than the demethoxy-analogue. In contrast to the 4-diazoacetylthianthren, 7-diazoacetyl-2-methylbenzo[*b*]thiophen with acetonitrile and perchloric acid cyclised in an alternative mode to give a new synthesis of 2-methyl-4-substituted oxazolium perchlorates.

REPLACING the nitrogen atom of pyridine by positively charged trivalent oxygen or sulphur atoms leads to the well known pyrylium and thiapyrylium ring systems, which are stable at low pH or in the presence of non-nucleophilic cations. Indolizine (1) bears a similar



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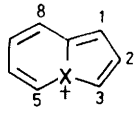
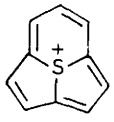


(2) X = O
(3) X = S
(4) X = S, 5,6,7,8-H

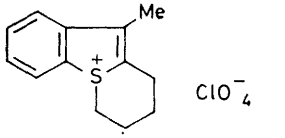


(5)

relationship to structures (2) and (3) which are not yet known. Zahradník,[1] using a simple Huckel-MO method which ignored participation of the sulphur 3*d* orbitals, showed that (3) and the sulphur analogue (5) of cycl-[3,2,2]azine should have high stability relative to similar structures where one or both of the five-membered rings had been expanded by vinyl units. It seems clearly worth while trying to synthesize these indolizine and cycl[3,2,2]azine analogues. The electron configuration round such a positively charged sulphur atom would be of significant interest. The slow inversion of a sulphur atom, as compared with nitrogen, when attached by single bonds to three carbon atoms, could imply that making the bonds from the sulphur atoms in (3) and (5) coplanar, so that maximum conjugation was possible, might not be so favourable energetically.

RESULTS AND DISCUSSION

Alkylation of the sulphur atom of a number of thiophens and benzo[*b*]thiophens takes place with trialkyloxonium tetrafluoroborates, with alkyl halides in the presence of silver perchlorate or tetrafluoroborate,[2,3] and with alkyl fluorosulphonates.[2,4] Only one sulphonium salt with the sulphur atom bridging an indolizine-like system has been described,[5] and this (6) was formed from 4-(3-methyl-2-benzo[*b*]thienyl)butyl iodide with silver perchlorate or hexafluorophosphate. The direction of the bond from the sulphur atom to the attached saturated carbon atom must be well away from the aromatic ring plane, as *X*-ray crystallographic studies have shown that this is the case for 1,2,3,5-tetramethylbenzo[*b*]thiophenium tetrafluoroborate[6] and 1-thiophenium bis-(methoxycarbonyl)methylide.[7] The object of the 3-methyl group in (6) was to prevent an alternative cyclisation at this position, but because *S*-alkylation seems the preferred route in the presence of silver salts [2] thiophen was converted by standard procedures into the iodide (7), in the hope of achieving cyclisation to (4). Neither this iodide, nor a number of related compounds (see Experimental section) could be cyclised by silver perchlorate, in agreement with the greater difficulty observed [2] in synthesising thiophenium, as compared with benzo[*b*]thiophenium salts.



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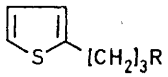
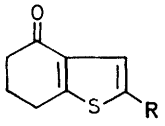


(7) R = CH_2I
(8) R = CO_2H

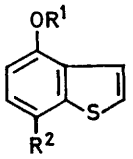


(9) R = H
(10) R = Ac

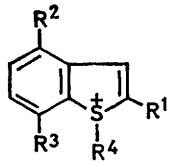
Scrowston [8] and Campaigne [9] have shown that 4-methoxybenzo[*b*]thiophen undergoes electrophilic substitution mainly at position 7, although a small amount can occur [8,10] at position 2, and the high yield in 7-acetylation [10] encouraged us to prepare (13), for attempted cyclisation to derivatives of (15).

The acid-catalysed cyclisation [11] of (8) in acetic anhydride on a small scale gave a high yield of the ketone (9) along with some (10), but increasing the scale greatly diminished the yield and an alternative synthesis [12] of (9) from cyclohexenone and 1,1-diethoxyethane-2-thiol, followed by chloranil oxidation, was no improvement. The reported [12] dehydrogenation of (9) to 4-hydroxybenzo[*b*]thiophen with sulphur in diphenyl ether gave only 17% yields, and palladium–charcoal [13] was no better. Methyl iodide and alkali effected a satisfactory conversion of (11) to (12) and the appropriate halogenoalkyl halides gave the bromo- (13) and chloro-ketones (14), the position of acylation being clear

from their n.m.r. spectra. All attempts to cyclise these compounds by silver perchlorate in the usual way to the thiophenium salt (15) failed.

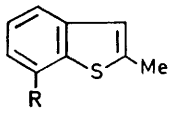


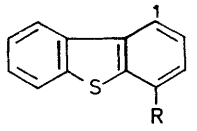
	R^1	R^2
(11)	H	H
(12)	Me	H
(13)	Me	$COCH_2Br$ or $COCH_2Cl$
(14)	Me	$COCH_2OH$



	R^1	R^2	R^3—R^4
(15)	H	OMe	$-COCH_2-$
(16)	Me	H	$-[CH_2]_2-$ or $-[CH_2]_3-$

7-Bromo-2-methylbenzo[*b*]thiophen (17) was now prepared by the thio-Claisen rearrangement procedure [14] using 2-bromophenyl 2-chloroprop-2-enyl sulphide. The corresponding Grignard reagent yielded the alcohols (18) and (19), which were converted *via* the toluene-*p*-sulphonates into the iodides (20) and (21). It can be argued that these iodides might have a better chance of cyclising to (16) than the halogeno-ketones to (15), but while silver iodide precipitated on treatment with silver perchlorate only ether-soluble products were formed. Both products showed close similarities in their n.m.r. spectra to their precursors, (20) and (21), except that one two-proton triplet had moved from *ca.* τ 6.6 and 7.0 to *ca.* τ 5.2 in both cases. This is at too low a field for the corresponding alcohols (τ 6.1 and 6.5, respectively) but is close to that expected for the methylene resonance of





(17) R = Br
(18) R = $-[CH_2]_2OH$
(19) R = $-[CH_2]_3OH$
(20) R = $-[CH_2]_2I$
(21) R = $-[CH_2]_3I$
(22) R = $-[CH_2]_2OClO_3$
(23) R = $-[CH_2]_3OClO_3$

(24) R = Li
(25) R = $-[CH_2]_2OH$

ethyl perchlorate, if one considers the resonance reported [15] for methyl perchlorate (τ 5.70 in CCl_4) and the usual [16] downfield shift (*ca.* 0.45) caused by the change of group. The products were therefore provisionally identified as (22) and (23) and not examined further because of the risk of explosion.

Lithiation of dibenzo[*b*,*d*]thiophen is reported [17] to occur at position 4, and (24) with oxiran gave (25). The couplings shown in the 270-MHz ^1H n.m.r. spectrum of (25) exclude the possibility of initial 2- or 3-lithiation, and comparison with the spectrum of dibenzo[*b*,*d*]-thiophen,[2] and assuming that the introduction of an alkyl group will cause upfield shifts, shows that the side-

TABLE 1

^1H N.m.r. spectra ($CDCl_3$ solutions τ scale, J in Hz)

Compound	Proton resonances
(7)	2.95—3.45 (ArH, m, H_3); 6.90 (1-H_2), app. t, $J_{1,2}$ 6); 7.20 (4-H_2, app. t, $J_{3,4}$ 6); 7.90—8.45 (2,3-H_4, m)
(10)	2.10 (3-H, s); 6.95 (5-H_2, app. t, $J_{5,6}$ 6); 7.20—8.00 (6,7-H_4, m); 7.50 (CH_3, s)
(13 Cl) [a]	1.85 (6-H, d, $J_{5,6}$ 9); 2.35 and 2.55 (2 3-H_2, pair of d's, $J_{2,3}$ 6); 5.00 ($COCH_2$, s); 5.95 (OCH_3, s)
(13 Br)	2.10 (6-H, d, $J_{5,6}$ 8); 2.55 (2,3-H_2, s); 3.30 (5-H, d); 5.55 ($COCH_2$, s); 6.05 (OCH_3, s)
(17)	2.50 (4-H, pair of d's $J_{4,5}$ 8, $J_{4,6}$ 1.5); 2.65 (6-H, pair of d's, $J_{5,6}$ 8); 2.85 (5-H, app. t); 3.05 (3-H, q, J_{3,CH_3} 1); 7.50 (CH_3, d)
(18)	2.55 (4′-H, pair of d's, $J_{4',5'}$ 7, $J_{4',6'}$ 2); 2.80 (5′-H, app. t, $J_{5',6'}$ 6); 3.05 (6′-H, pair of d's); 3.10 (3′-H, q, J_{3',CH_3} 1); 6.10 (1-H_2, t, $J_{1,2}$ 6); 7.00 (2-H_2, t); 7.50 (CH_3, d); 8.30 (OH, s)
(19) [b]	2.70 (4′-H, pair of d's, $J_{4',5'}$ 7, $J_{4',6'}$ 2); 2.95 (5′-H, app. t, $J_{5',6'}$ 6); 3.15 (6′-H, pair of d's); 3.20 (3′-H, q, J_{3',CH_3} 1); 6.50 (1-H_2, t, $J_{1,2}$ 7); 6.65 (OH, s); 7.20 (3-H_2, t, $J_{2,3}$ 8); 7.50 (CH_3, d); 8.15 (2-H_2, app. q)
(20) [a]	2.45 (4′-H, pair of d's, $J_{4',5'}$ 8, $J_{4',6'}$ 2); 2.75, (5′-H, app. t, $J_{5',6'}$ 7); 2.95 (6′-H, pair of d's); 3.00 (3′-H, q, J_{3,CH_3} 1); 6.60 (1,2-H_4, m); 7.50 (CH_3, d)
(21) [b]	2.65 (4′-H, pair of d's, $J_{4',5'}$ 7, $J_{4',6'}$ 2); 2.90 (5′-H, app. t, $J_{5',6'}$ 7); 3.05 (6′-H, pair of d's); 3.15 (3′-H, q, J_{3',CH_3} 1); 6.95 and 7.15 (1,3-H_4, pair of t's, $J_{1,2}$ and $J_{2,3}$ 6); 7.50 (CH_3, d); 7.75 (2-H_2, app. q)
(25) [c]	1.95—2.00 (9-H, m); 2.06 (1-H, d, $J_{1,2}$ 8); 2.23—2.25 (6-H, m); 2.61—2.65 (7,8-H_2, m); 2.67 (2-H, app. t); 2.75 (3-H, d, $J_{2,3}$ 8); 6.05 (1-H_2, t, $J_{1,2}$ 7); 6.93 (2-H_2, t); 7.30 (OH, s)
(26) [d]	1.65—2.15 (ArH, m, H_4); 5.35 and 5.75 (2-H_2, pair of d's, $J_{2,2}$ 18); 6.85 (SCH_3, s)
(27) [d]	1.75—2.30 (ArH, m, H_4); 3.85 (2-H s); 5.90 (OCH_3, s); 6.85 (SCH_3, s)
(29)	2.30—3.00 (ArH, m, H_7); 4.40 (COCH, s)
(30) [e]	1.65—2.45 (ArH, m, H_7); 4.90 (CH_2, s)
(31) [f]	1.80—2.45 (ArH, m, H_7); 3.10 (1-H, s); 5.65 (OCH_3, s)
(32) [f]	1.65—2.40 (ArH, m, H_7); 2.50 (vinyl H, s, H); 6.35 ($SOCH_3$, s); 6.65 (OCH_3, s)
(35) [e]	2.10 (4-H, s); 2.20 [g] (NH); 2.15 and 2.30 (4′,6′-H_2, both pairs of d's, $J_{4',5'}$ and $J_{5',6'}$ 7, $J_{4',6'}$ 2); 2.45 (5′-H, app. t); 2.85 (3′-H, q, J_{3',CH_3} 1); 7.10 (2-CH_3, s); 7.40 (2-CH_3, d)
(35) free base	2.30—2.85 (4′,5′,6′-H_3, m); 2.50 (4-H, s); 3.00 (3′-H, q, J_{3',CH_3} 1); 7.40 (2′-CH_3, d); 7.45 (2-CH_3, s)
(37)	1.60 (3-H, d, $J_{3,4}$ 6); 1.75—2.30 (5,6,9-H_3, m); 2.35—2.65 (4,7,8-H_3, m); 4.95 (1-H_2, s)
(36) [e]	1.65—2.65 (ArH, m, H_7); 2.10 (4-H, s); 6.10 (NH, br); 7.10 (2-CH_3, s)
(36) free base	1.75—2.95 (ArH, m, H_7); 2.75 (4′-H, s); 7.45 2′-CH_3 s)
(38)	1.80—2.95 (ArH, m H_8); 2.25 (vinyl-H, s, H_1)
(39)	1.60 (vinyl-H, s, H_1); 2.00—2.80 (ArH, m, H_8); 5.90 (OCH_3, s)

[a] Solvent $(CD_3)_2CO$. [b] Solvent CCl_4. [c] Recorded at 270 MHz in $CDCl_3$/10% $(CD_3)_2SO$. [d] Solvent CD_3OD. [e] Recorded in CD_3CN. [f] Recorded in CD_3NO_2. [g] Estimated position, exchanges with D_2O.

TABLE 2

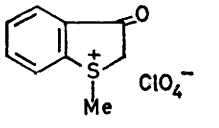
Analytical data

Compound	Found (%) C	H	Other	Molecular formula	Calculated (%) C	H	Other
4-(2-Thienyl)butyrolactone	56.9	4.8	19.3 [a]	$C_8H_8O_2S$	57.1	4.8	19.0 [a]
4-(2-Thienyl)butyl *p*-toluenesulphonate	57.9	6.0		$C_{15}H_{18}O_3S_2$	58.1	5.9	
(7)	36.5	4.2		$C_8H_{11}IS$	36.1	4.1	
3-Hydroxypropyl 2-thienyl ketone	56.4	6.0	18.5 [a]	$C_8H_{10}O_2S$	56.5	5.9	18.8 [a]
2,4-Dinitrophenylhydrazone of above	48.0	4.2		$C_{14}H_{14}N_4O_5S$	48.0	4.0	
3-Iodopropyl 2-thienyl ketone			45.5 [b]	C_8H_9IOS			45.3 [b]
(10)	61.9	5.2	16.6 [a]	$C_{10}H_{10}O_2S$	61.9	5.2	16.5 [a]
2,4-Dinitrophenylhydrazone of (10)	51.5	3.7	14.9 [c]	$C_{16}H_{14}N_4O_5S$	51.3	3.8	15.0 [c]
(13, Cl)	55.1	3.8		$C_{11}H_9ClO_2S$	54.9	3.7	
2-Bromophenyl 2-chloroprop-2-enyl sulphide	41.1	3.2		C_9H_8BrClS	41.0	3.0	
(17)	47.6	3.1		C_9H_7BrS	47.4	3.1	
(18)	68.5	6.3		$C_{11}H_{12}OS$	68.7	6.3	
p-Toluenesulphonate of (18)	62.5	5.3		$C_{18}H_{18}O_3S_2$	62.4	5.2	
1,1-Dioxide of (18)	39.4	3.4		$C_{11}H_{11}IO_2S$	39.5	3.3	
(19)	69.9	6.6		$C_{12}H_{14}OS$	69.9	6.8	
p-Toluenesulphonate of (19)	63.0	5.6		$C_{19}H_{20}O_3S_2$	63.3	5.6	
(20)	43.7	3.5		$C_{11}H_{11}IS$	43.7	3.7	
(21)	46.0	4.2		$C_{12}H_{13}IS$	45.6	4.1	
(25)	73.5	5.5		$C_{14}H_{12}OS$	73.8	5.3	
p-Toluenesulphonate of (25)	66.0	4.9		$C_{21}H_{18}O_3S_2$	66.0	4.7	
Iodide from (25)	50.1	3.4		$C_{14}H_{11}IS$	49.7	3.3	
1-Oxide of above	47.7	3.2	9.0 [a]	$C_{14}H_{11}IOS$	47.5	4.1	9.1 [a]
4-Methylthiophenacyl chloride	54.1	4.6		C_9H_9ClOS	53.9	4.5	
(26)	40.9	3.4	12.1 [a]	$C_9H_9ClO_5S$	40.9	3.7	11.7 [a]
(26) picrate	45.8	2.7	10.5 [c]	$C_{15}H_{11}N_3O_8S$	45.8	2.8	10.7 [c]
5-Me-(26), but hexafluorophosphate	32.5	3.1	8.7 [a]	$C_{10}H_{11}F_6OPS\cdot 0.25\ KPF_6$	32.3	3.0	8.8 [a]
5-Me-(26)	43.3	4.1		$C_{10}H_{11}ClO_5S$	43.1	4.0	
(27)	43.3	3.8	10.9 [a]	$C_{10}H_{11}ClO_5S$	43.1	4.0	11.5 [a]
5-Me-(27), but hexafluorophosphate	34.5	3.5		$C_{11}H_{13}F_6OPS\cdot 0.25\ KPF_6$	34.2	3.4	
(27), 5-Me	45.4	4.6		$C_{11}H_{13}ClO_5S$	45.1	4.5	
(30)	47.2	2.7	18.2 [a]	$C_{14}H_9ClO_5S_2$	47.1	2.5	18.0 [a]
(31)	48.7	3.1	17.0 [a]	$C_{15}H_{11}ClO_5S_2$	48.6	3.0	17.3 [a]
(32)	40.2	3.2	13.1 [a]	$C_{16}H_{14}BrClO_6S_2$	39.9	2.9	13.3 [a]
2-Methylbenzo[*b*]thiophen-7-carboxylic acid	62.4	4.3	16.5 [a]	$C_{10}H_8O_2S$	62.5	4.2	16.7 [a]
(35)	47.4	3.6	10.0 [a]	$C_{13}H_{12}ClNO_5S$	47.4	3.7	9.7 [a]
(35), base (not salt)			5.9 [c]	$C_{13}H_{11}NOS$			6.1 [c]
(36)	52.6	3.5	3.9 [c]	$C_{16}H_{12}ClNO_5S$	52.5	3.3	3.8 [c]
(38)	65.8	3.4	20.2 [a]	$C_{17}H_{10}O_2S_2$	65.8	3.2	20.6 [a]
(39)	66.7	4.7	19.7 [a]	$C_{18}H_{12}O_2S_2$	66.3	4.3	19.6 [a]
bis-(4-dibenzo[*b*,*d*]thienylethyl)methanol	73.3	5.0	14.6 [a]	$C_{26}H_{18}OS_2$	73.3	5.0	14.5 [a]

[a] S. [b] I. [c] N.

chain can only be placed at position 4. This alcohol was converted into the iodide and this iodide, and the corresponding 5-oxide obtained with hydrogen peroxide, again gave only alkyl perchlorates on treatment with silver perchlorate. In contrast to 2-dibenzo[*b*,*d*]-thienyl-lithium,[18] (24) did not react with *NN*-dimethylacetamide, nor with acetonitrile or acetyl chloride, to give a significant quantity of the 4-acetyl derivative, even though carbon dioxide gave the known [17] 4-carboxylic acid and a large excess of ethyl acetate gave bis-[2-(4-dibenzo[*b*,*d*]thienyl)ethyl]methanol.

Flowers *et al.*[19] have shown that ω-diazo-2-phenylthioacetophenones with perchloric acid in acetonitrile give 1-phenyl-3-oxo-2*H*-benzo[*b*]thiophenium perchlorates, and we have now found that methyl iodide and silver perchlorate with 3-methoxybenzo[*b*]thiophen causes both *S*-methylation and *O*-demethylation to give a similar product (26); no 1-alkylation of 2-hydroxy-,[20] 2-methoxy-,[21] or 2-t-butoxy-thiophen [22] took place under similar conditions. The same cation (26), isolated as the picrate, was also prepared from thioanisole, chloroacetyl chloride, and aluminium chloride by an adaptation of a literature procedure.[23] The diastereotopic methylene protons of (26) showed as an AB system (*J* 18 Hz) in the ^{1}H n.m.r. spectrum. Treatment with diazomethane gave the 3-methoxy-derivative (27), in which much resonance-stabilisation involving (28) must occur. In the ^{1}H n.m.r. spectrum the 1-methyl resonance appears



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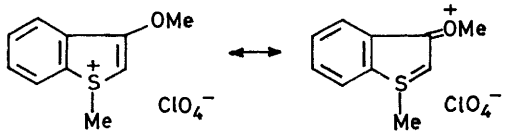
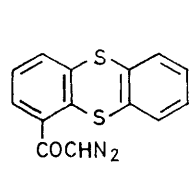


(27) (28)

at higher field than that of 1-methylbenzo[*b*]thiophenium perchlorate [2] and the *O*-methyl resonance is at unusually low field; and (26), unlike the demethoxy-analogue,[2] does not lose the 1-methyl group detectably in methanol

at room temperature over 24 h. The importance of charge delocalisation from sulphur to the 3-position has also been shown [4] for 1,2,3,4,5-pentamethylthiophenium fluorosulphonate by ^{13}C n.m.r. chemical-shift studies.[4] It was therefore decided to combine Flowers approach with a subsequent methylation to try to obtain a stable bridged thiophenium salt.

1-Diazoacetylthianthren (29) was prepared by standard methods, and identified from its spectra. On treatment with aqueous perchloric acid in acetonitrile polymeric material was deposited, but ether subsequently precipitated the salt (30), which showed a carbonyl



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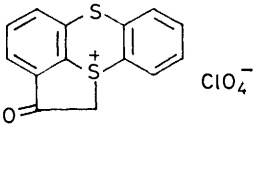

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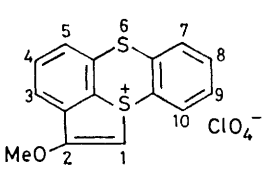
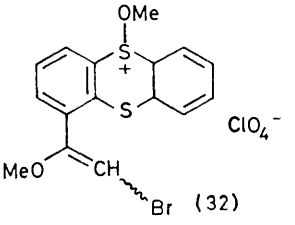


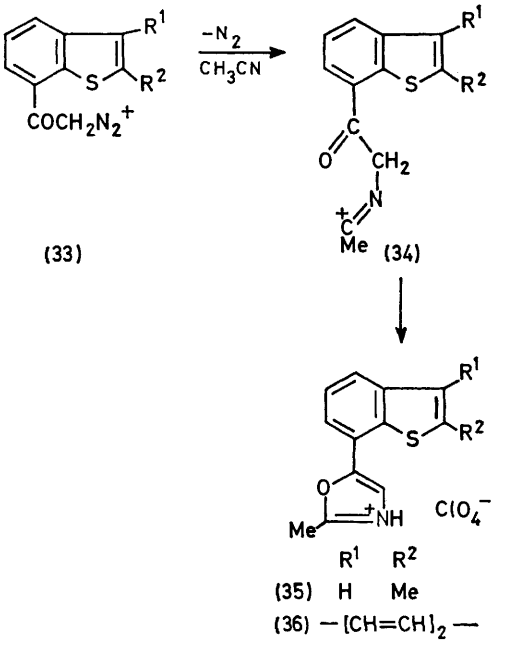
(31)



(32)

absorption at 1 735 cm^{-1}. The ^1H n.m.r. spectrum showed the methylene protons as a singlet, in contrast to those of the salt (26). This is more likely to be due to the protons being accidentally magnetically equivalent in (30) than the molecule being planar. With diazomethane the perchlorate (31) was formed and no carbonyl absorption was now present. The ^1H n.m.r. resonances for the 1-proton and the methoxy-group are at significantly lower field than those for the comparable protons of (27). This may be due in part to the change in solvent from $[^2H_3]$nitromethane to acetonitrile, but the large shift (τ 0.75) for the 1 proton of (31) could be related to its closeness to the edge of the neighbouring benzene ring. The salt (31) was unchanged by methanol or bromine in chloroform at room temperature, unlike 1-methylbenzo[*b*]thiophenium perchlorate which reacted with both,[2] but a mixture of bromine and methanol added on the elements of methyl hypobromite. The new compound showed *O*-methyl resonances at τ 6.65 and 6.35 and a single proton at τ 2.50, so there was no doubt that the original five-membered ring had been affected. Structure (32), or an isomer where the 5-methoxy-group is placed on the alternative sulphur atom, fit the spectral data for this product.

7-Bromo-2-methylbenzo[*b*]thiophen (17) was now converted into the 7-diazomethyl ketone by standard procedures, and its identity confirmed by conversion to the 7-hydroxymethyl ketone, by aqueous perchloric acid. Treatment of the diazoketone with perchloric acid in acetonitrile was anticipated to give a tricyclic analogue of (30), but the crystalline product showed N–H absorption and no carbonyl absorption in the i.r. The ^1H n.m.r. spectrum showed resonances corresponding to a 7-substituted 2-methylbenzo[*b*]thiophenium system with the addition of two singlets integrating for 1 and 3 protons, respectively, and in the free base, formed with sodium carbonate, these moved *ca.* 0.4 τ upfield, the rest of the spectrum being unchanged. Cyclisation to the oxazolium salt (35) had therefore taken place. It seems likely that protonation of the diazoketone to give a diazonium salt (33) is followed (Scheme) by loss of nitrogen, attack of the resultant carbonium ion on the acetonitrile giving (34), and cyclisation. A similar

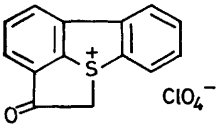


SCHEME

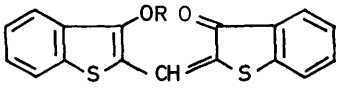
reaction took place with 4-diazoacetyldibenzo[*b*,*d*]-thiophen but here the oxazolium salt (36), on one occasion, was accompanied by another substance, which was unchanged on refluxing in acetonitrile. The substance may have been a mixture of (36) and (37), as suggested by its ^1H n.m.r. spectrum which showed the expected similarities with that of (30), or it may have been 5-(4-dibenzothienyl)-3-[2-(4-dibenzothienyl)-2-oxoethyl]-2-methyloxazolium perchlorate. The easy synthesis of these oxazolium salts appears to be unprecedented, although heating diazoacetophenone with benzonitrile to 145 °C gives 2,5-diphenylisoxazole in what could be concerted cyclisation.[24,25] The formation of oxazoles from nitrilium salts [*cf.* (34)] obtained in other ways is, however, well known.[26]

In the synthesis of 3-methoxybenzo[*b*]thiophen from 3-bromobenzothiophen and sodium methoxide, a red compound was also isolated. This was identified as (38) from its spectra, and from the spectral data for (39), which was formed with diazomethane. This compound (38), also converted into its methyl derivative (39) but with methyl iodide and alkali, has been obtained before [27]

from 3-oxo-2*H*-benzo[*b*]thiophen and various formic acid derivatives. It could have been built up similarly in our preparation as air was not excluded and some oxidation of the methoxide could have taken place.



(37)



(38) R = H
(39) R = H

EXPERIMENTAL

The instruments and general procedures employed have been described.[28,29] ^{1}H N.m.r. and i.r. spectra for most of the compounds mentioned are available.[29]

4-(2-*Thienyl*)*butyrolactone*.—Sodium borohydride (1.4 g) in water (80 ml) was added dropwise with stirring and cooling to 4-oxo-4-(2-thienyl)butanoic acid (21 g) (prepared as described [30] and having the lit.[31] m.p.) in 2% aqueous sodium hydroxide (250 ml) and maintained at 60 °C for 6 h. The solution was acidified (HCl aqueous), extracted with ether, and distillation of the dried extract gave 4-(2-*thienyl*)*butyrolactone* (15 g) as a pale yellow liquid, b.p. 120—130 °C at 0.25 mmHg. A satisfactory lithium aluminium hydride reduction of this to 1-(2-thienyl)butane-1,4-diol could not be effected.

4-(2-*Thienyl*)*butanoic Acid* (8).—4-Oxo-4-(2-thienyl)-butanoic acid (17 g) and concentrated hydrochloric acid (300 ml) were added to zinc turnings (170 g, previously treated with 500 ml of 5% aqueous mercuric chloride) cooled in ice. When the solution reached room temperature, concentrated hydrochloric acid (100 ml) was added over 50 h, and the mixture was refluxed (35 min), then cooled and extracted with ether. Distillation of the dried extract gave the acid (8) (10 g, 72%), b.p. 123—126 °C at 0.2 mmHg (lit.,[32] 130—134 °C at 0.15 mmHg). Only a 40% yield was obtained on a four-fold scale. Reduction using hydrazine hydrate with ethylene glycol (500 ml) containing previously dissolved potassium hydroxide gave a 40% yield instead of the 91% reported earlier.[33]

4-(2-*Thienyl*)*butyl Iodide*.—4-(2-Thienyl)butanoic acid (2.0 g) in dry ether (30 ml) was added dropwise with cooling and stirring to lithium aluminium hydride (0.5 g) in dry ether (30 ml). After 15 min the solution was refluxed for 16 h and ethyl acetate (1 g) added. The mixture was treated with ammonium chloride (7 g) in ice–water (100 ml), extracted with ether, and evaporation of the washed ($NaHCO_3$ aqueous) dried extract gave 4-(2-thienyl)butanol (1.9 g, 100%) as a pale yellow liquid; no impurities were detectable in its ^{1}H n.m.r. spectrum. The alcohol (5.0 g) was dissolved in dry pyridine (20 ml) at 0 °C and *p*-toluenesulphonyl chloride (12 g) added. After 48 h at 0 °C, the mixture was added to ice–water (200 ml) and extracted with ether. The washed (2M-hydrochloric acid, 2 × 50 ml) dried extract was evaporated at room temperature to an oil which recrystallised at low temperature (solid CO_2 cooling) from light petroleum to give 4-(2-*thienyl*)*butyl* p-*toluenesulphonate*, colourless crystals (7.1 g), m.p. 28.5—29.5 °C. The *p*-toluenesulphonate (7 g) was refluxed with potassium iodide (7 g) in acetone (100 ml) for 4 h. Water (300 ml) was added and the mixture extracted with ether. Distillation of the dried extract gave 4-(2-*thienyl*)*butyl iodide* as a pale yellow liquid (4 g), b.p. 80—85 °C at 0.1 mmHg.

1-(2-*Thienyl*)*butane*-1,4-*diol*.— 4-Oxo-4-(2-thienyl)-butanoic acid (15 g) suspended in dry ether (200 ml) was added to lithium aluminium hydride (5 g) in dry ether (200 ml) with cooling and stirring. After refluxing for 17 h, ethyl acetate (10 ml) was added and the mixture poured into ammonium chloride (50 g) in water (500 ml). The diol (11.2 g) was extracted with ether and had m.p. 44—49 °C (lit.,[34] 46—48 °C).

3-*Hydroxypropyl* 2-*Thienyl Ketone*.—1-(2-Thienyl)butane-1,4-diol (11.2 g) and active manganese dioxide [35] (110 g) were stirred in dichloromethane (250 ml) for 24 h. The solution was filtered and distilled to give 3-*hydroxypropyl* 2-*thienyl ketone* as a pale yellow liquid (8 g), b.p. 128—135 °C at 0.2 mmHg. Chromium trioxide and pyridine in dichloromethane gave a much lower yield. The 2,4-*dinitrophenylhydrazone*, orange crystals from methanol, had m.p. 160.5—162 °C.

3-*Iodopropyl* 2-*Thienyl Ketone*.—*p*-Toluenesulphonyl chloride (6.05 g) was added to the above alcohol (5.4 g) in dry pyridine (18 ml) at 0 °C. After 24 h at 0 °C the mixture was poured into ice–water (200 ml) with stirring to give 3-(*p*-toluenesulphonyl)propyl 2-thienyl ketone as colourless crystals (8.5 g), m.p. 50—60 °C. This compound (7 g) was refluxed with potassium iodide (7 g) in acetone (50 ml) for 8 h. Water (250 ml) was added and the solution extracted with ether. The ether solution was dried and distilled to give 3-*iodopropyl* 2-*thienyl ketone* as a pale yellow oil, b.p. 116—120 °C at 0.1 mmHg, (3 g), slowly solidifying, m.p. 32—37 °C.

(2-*Thienylthio*)*acetaldehyde Diethyl Acetal*.—Thiophen-2-thiol (13.8 g) [36] was added with stirring to sodium (2.7 g) dissolving in ethanol (50 ml). Bromoacetaldehyde diethyl acetal (23.4 g) was added, and the mixture refluxed for 4.5 h, filtered, solvent removed, and water (200 ml) added. Ether extraction gave (2-thienylthio)acetaldehyde diethyl acetal (25 g, 91%) as a colourless liquid, b.p. 75—85 °C at 0.2 mmHg, pure by ^{1}H n.m.r. spectroscopy. A good elemental analysis could not be obtained because of a small amount of decomposition on distillation.

Attempted S-*Alkylations*.—4-(2-Thienyl)butyl iodide and *p*-toluenesulphonate, 3-iodopropyl 2-thienyl ketone, and 2-methoxy, 2-hydroxy-, and 2-t-butoxy-thiophen mixed with methyl iodide were treated with silver perchlorate in dichloromethane [2] in the dark at room temperature to −20 °C. No indication (^{1}H n.m.r.) for *S*-alkylation was obtained and no crystalline products were isolable. (2-Thienylthio)acetaldehyde diethyl acetal gave an amorphous mass with 60% perchloric acid, alone or in dichloromethane, with or without silver perchlorate; no n.m.r. evidence for *S*-alkylation was obtained.

6,7-*Dihydrobenzo*[b]*thiophen*-4(5H)-*one* (9).—4-(2-Thienyl)butanoic acid (80 g) and orthophosphoric acid (1.9 ml) in acetic anhydride (80 ml) were maintained at 120—140 °C for 3 h, cooled, and added to water (700 ml). The solution was neutralised with sodium carbonate and extracted with chloroform. The extract was dried and distilled to give (9) (61 g, 85%), b.p. 88 °C at 0.35 mmHg (lit.,[11] 125—130 °C at 7 mmHg), which could not be induced

to crystallise (lit.,[11,33] m.p. 25—36 °C), and 2-*acetyl*-6,7-*dihydrobenzo*[b]*thiophen*-4(5H)-*one* (10), b.p. 120—145 °C at 0.5 mmHg, which recrystallised from methanol as colourless needles (5.1 g), m.p. 87—88 °C; *m/e* 196 ($M^+ + 2$) (4%), 195 ($M^+ + 1$) (10), 194 (M^+) (73), 180 (11), 179 (100), 166 (46), 138 (32), 95 (28), 51 (11), 45 (11) and 43 (40); *m** 165.5, 142.1, and 114.8; the 2,4-*dinitrophenylhydrazone* had m.p. 227—240 °C (decomp.).

4-*Methoxybenzo*[b]*thiophen* (12).—This was obtained[10] from the phenol[12] (11), methyl iodide, and potassium hydroxide, as an oil, b.p. 73—83 °C at 0.15 mmHg (lit.,[36] b.p. 141 °C 17 mmHg) in 62% yield.

7-*Chloroacetyl*-4-*methoxybenzo*(b)*thiophen* (13).—4-Methoxybenzo[*b*]thiophen (1 g), chloroacetyl chloride (0.75 g), and anhydrous aluminium chloride were refluxed in dichloromethane (20 ml) for 30 min. Water (30 ml) was added and the mixture extracted with chloroform. The chloroform solution was dried and evaporated, and the residue extracted with hot ethanol. The ethanol-soluble material was recrystallised from methanol to give 7-*chloroacetyl*-4-*methoxybenzo*[b]*thiophen* as colourless needles (0.4 g), m.p. 140—142 °C. Repetition of the procedure using bromoacetyl bromide (0.55 ml) gave the 7-bromoacetyl analogue (13) as colourless crystals (0.2 g) from methanol, m.p. 116—127 °C.

2-*Chloroprop*-2-*enyl* 2-*Bromophenyl Sulphide*.—2-Bromobenzenethiol (26.5 g), 2,3-dichloroprop-1-ene (15.0 g), and potassium carbonate (23.9 g) were refluxed in acetone (60 ml) for 15 h. The residue from solvent removal was dissolved in water (1 l) and extracted with ether. The organic phase was washed with 5% aqueous sodium hydroxide (200 ml), dried, and distilled to give 2-*chloroprop*-2-*enyl* 2-*bromophenyl sulphide* (28.2 g) as a colourless liquid, b.p. 106—110 °C at 0.3 mmHg.

7-*Bromo*-2-*methylbenzo*[b]*thiophen* (17).—The above sulphide (26.5 g) was refluxed in *NN*-diethylaniline (100 ml) for 24 h under nitrogen. The solution was cooled and ether (500 ml) added. The organic phase was extracted with 10% hydrochloric acid (4 × 800 ml), dried, and distilled to give 7-*bromo*-2-*methylbenzo*[b]*thiophen* as a colourless liquid (8.8 g), b.p. 94—100 °C at 0.2 mmHg.

7-(2-*Hydroxyethyl*)-2-*methylbenzo*[b]*thiophen* (18).—The bromo-compound (17) (18 g) in methyl iodide (26 g) was added dropwise to magnesium turnings (12 g) in dry ether (200 ml) so that a steady reflux was maintained. After addition was complete the solution was refluxed for 45 min. Oxiran (6.5 g) in dry ether (15 ml) was added to the solution, cooled in ice–water, during 5 min with stirring. After 1 h dry benzene (75 ml) was added and the ether distilled off. The solution was refluxed for 30 min and dilute aqueous hydrochloric acid added. The benzene layer was separated and the aqueous layer extracted once with ether. The combined extracts were dried and distilled to give (17) (3.8 g), b.p. 90—125 °C at 0.3 mmHg and 7-(2-*hydroxyethyl*)-2-*methylbenzo*[b]*thiophen* (18), b.p. 126—141 °C at 0.3 mmHg, which crystallised from toluene–light petroleum as colourless crystals (9.0 g), m.p. 35—37 °C.

7-(3-*Hydroxypropyl*)-2-*methylbenzo*[b]*thiophen* (19).—The bromo-compound (17) (3.85 g) and methyl iodide (2.4 g) were added to magnesium turnings (1.35 g) in dry ether (100 ml) so that a steady reflux was maintained. Methyl iodide (2.4 g) was added again to maintain a reflux. The procedure for (18) but using oxetan instead of oxiran then gave 2-*methyl*-7-(3-*hydroxypropyl*)*benzo*[b]*thiophen* (1.50 g) as a colourless liquid, b.p. 126—135 °C at 0.05 mmHg.

p-*Toluenesulphonates of* (18) *and* (19).—The alcohols (18) or (19) (1.4 g) in dry pyridine (10 ml) was treated with *p*-toluenesulphonyl chloride (3 g) at 0 °C and left for 36 h at 0 °C. The mixture was poured into ice–water (150 ml) and ether-extracted. The organic phase was dried and the residue after removal of solvent recrystallised to give 2-*methyl*-7-(2-p-*toluenesulphonylethyl*)*benzo*[b]*thiophen* (1.9 g), m.p. 58—60 °C, or 2-*methyl*-7-(3-p-*toluenesulphonylpropyl*)-*benzo*[b]*thiophen* (0.95 g), m.p. 56—60° C, as colourless crystals from light petroleum.

The (2-*Iodoethyl*)- *and* (3-*Iodopropyl*)-*benzo*[b]*thiophens* (20) *and* (21).—The appropriate *p*-toluenesulphonate (above) (0.95 g) was refluxed with potassium iodide (1.2 g) in acetone (20 ml) for 9 h. The mixture was poured into water (100 ml) and ether-extracted. The organic phase was dried and distilled to give 7-(2-*iodoethyl*)-2-*methylbenzo*[b]*thiophen* (20) (0.71 g), b.p. 120—125 °C at 0.05 mmHg, and 7-(3-*iodopropyl*)-2-*methylbenzo*[b]*thiophen* (21) (0.52 g), b.p. 136—140 °C at 0.05 mmHg, both as pale yellow liquids.

7-(2-*Iodoethyl*)-2-*methylbenzo*[b]*thiophen* 1,1-*Dioxide*.—The iodide (20) (1 g), 30% hydrogen peroxide (3 ml) and glacial acetic acid (4 ml) were maintained at 70 °C for 1 h and added to water (50 ml). Chromatography of the chloroform-soluble fraction on alumina and elution with toluene gave, in order, the starting iodide (0.2 g), and a second band which was recrystallised from methanol to give 7-(2-*iodoethyl*)-2-*methylbenzo*[b]*thiophen* 1,1-*dioxide* as pink crystals (0.4 g), m.p. 112—115 °C; *m/e* 335 ($M^+ + 1$) (2%), 334 (M^+) (13), 208 (15), 207 (100), 158 (11), 135 (11), 128 (21), 115 (22), 91 (12), 43 (15), 32 (23), and 28 (81); *m** 128.1.

4-(2-*Iodoethyl*)*dibenzo*[b,d]*thiophen* (25).—4-Dibenzo[*b,d*]-thienyl-lithium[17] from dibenzo[*b,d*]thiophen (8 g) was treated with oxiran (7 g) at 5 °C. A vigorous reaction which ejected material out of the condenser ensued. After stirring at room temperature for 8 h the procedure used for (18) was repeated to give 4-(2-*hydroxyethyl*)*dibenzo*[b,d]-*thiophen* (25) as colourless crystals (2.8 g) from light petroleum, m.p. 69—76 °C.

This compound (2.5 g), using the procedure for (18), gave 4-(2-p-*toluenesulphonylethyl*)*dibenzo*[b,d]*thiophen* as colourless crystals (4 g) from chloroform–methanol, m.p. 98—101 °C. This compound (6.8 g) gave 4-(2-*iodoethyl*)*dibenzo*-[b,d]*thiophen*, using the procedure for (20), as colourless crystals (5.5 g) from light petroleum–toluene, m.p. 79—83 °C.

The last compound (1.35 g) was refluxed with 30% hydrogen peroxide (8 ml) in glacial acetic acid (10 ml) for 20 min and added to water (150 ml). The mixture was extracted with chloroform and the organic phase dried. The residue from solvent removal was recrystallised from ethanol to give 4-(2-*iodoethyl*)*dibenzo*[b,d]*thiophen* 5-*oxide* as colourless crystals (0.6 g), m.p. 116—120 °C; *m/e* 355 ($M^+ + 1$) (2%), 354 (M^+) (15), 243 (15), 227 (13), 212 (17), 211 (100), 210 (27), 209 (11), 208 (16), 197 (18), 185 (10), 184 (30), 178 (24), 165 (11), and 139 (21); *m** 131.8, 149.9.

Reaction of (20), (21), 4-(2-*Iodoethyl*)*dibenzo*[d,b]*thiophen and its* 5-*Oxide with Silver Perchlorate*.—The iodide (0.01 mol) was stirred with silver perchlorate (0.01 mol) in 1,2-dichloroethane (30 ml) in the dark for 18 h. The solution was filtered and solvent removed *in vacuo* at room temperature to give an oil. The ^1H n.m.r. spectra (CD_3CN) for the first three iodides showed that only the corresponding alkyl perchlorates had been formed. For the 5-oxide the spectrum showed a mixture of starting material and alkyl perchlorate.

Bis-{2-(4-*dibenzo*[b,d]*thienyl*)*ethyl*}*methanol*.— 4-Dibenzo-[*b,d*]thienyl-lithium from dibenzo[*b,d*]thiophen (8 g) was treated with redistilled ethyl acetate (10 ml) at 40 °C with vigorous stirring and refluxed for 2 h. The mixture was acidified and ether-extracted. The organic layer was dried and the residue from solvent removal extracted with hot light petroleum (3 × 50 ml). The residue was chromatographed on alumina, eluting with toluene. Dibenzo[*b,d*]-thiophen (3 g) was eluted first, followed by *bis*-{2-(4-*dibenzo*-[b,d]*thienyl*)*ethyl*}*methanol* (3 g), colourless crystals from chloroform–methanol, m.p. 109—113 °C; *m/e* 412 (M^+ + 2) (2%), 411 (M^+ + 1) (8), 410 (M^+) (23), 395 (22), 394 (22), 393 (31), 392 (100), 391 (25), 390 (25), 358 (13), 211 (39), 196 (16), 195 (13), 188 (15), 184 (34), 183 (19), 139 (10), 87 (15), 85 (39), 83 (88), 49 (19), 48 (19), 47 (40), 43 (20), and 40 (13); *m** 380.5.

3-*Methoxybenzo*[b]*thiophen*.—3-Bromobenzo[*b*]thiophen [37] (20 g) was refluxed with cupric oxide (4 g) and potassium iodide (0.15 g) in methanol (90 ml) containing previously dissolved sodium (6 g) for 120 h. Water (200 ml) and ether (200 ml) were added and the solution filtered. The mixture was acidified (HCl) to precipitate 2-{(3-hydroxybenzo[*b*]-thiophen-2-yl)methylene}benzo[*b*]thiophen-3(2*H*)-one (38), red needles from acetone (0.5 g), m.p. 252—257 °C (lit.,[27] m.p. 270 °C). The filtrate was ether-extracted and the organic layer dried and distilled to give a mixture of 3-bromo- and 3-methoxy-benzo[*b*]thiophen, b.p. 60—95 °C at 0.2 mmHg, (7.5 g) and 3-methoxybenzo[*b*]thiophen (2.5 g), b.p. 95—100 °C at 0.2 mmHg (lit.,[38] 107—108.5 °C at 3 mmHg).

The ketone (38) (0.1 g) was suspended in ether (10 ml) and diazomethane (0.13 g) in ether (5 ml) added. The suspension was left for 18 h and the solvent then removed *in vacuo*. The residue was recrystallised from methanol–chloroform to give 2-[(3-methoxybenzo[*b*]thiophen-2-yl)methylene]benzo-[*b*]thiophen-3(2 *H*)-one (39) as orange crystals (0.1 g), m.p. 224—229 °C (lit.,[27] 218—220 °C).

Reaction of 3-*Methoxybenzo*[b]*thiophen with Methyl Iodide*.—Methyl iodide (3.5 g) in 1,2-dichloroethane (10 ml) was added with stirring to 3-methoxybenzo[*b*]thiophen (15 g) and silver perchlorate (1.75 g) in 1,2-dichloroethane (30 ml) and stirred in the dark for 15 h. The solution was filtered and the solvent removed *in vacuo* at room temperature to give an oil which crystallised on the addition of chloroform. Recrystallisation from acetonitrile–ether at −20 °C gave 1-*methyl*-3(2H)-*oxobenzo*[b]*thiophen perchlorate* (26) as colourless crystals (0.21 g), m.p. 161—163.5 °C. Repetition using ethyl iodide instead of methyl iodide, and with 1,3-dibromopropane gave a crude product, the n.m.r. spectrum (CD_3CN) of which showed no trace of *S*-alkylation.

3-*Methoxy*-1-*methylbenzo*[b]*thiophenium Perchlorate*.—Diazomethane (0.05 g) in ether (2 ml) was added to (26) (0.21 g) in dry acetonitrile (10 ml) at 0 °C and left for 4 h. After the reaction had stood overnight at room temperature dry ether (50 ml) was added to give 3-*methoxy*-1-*methylbenzo*[b]-*thiophenium perchlorate*, pale yellow crystals (0.04 g), m.p. 138—141 °C.

1-*Methyl*-3(2H)-*oxobenzo*[b]*thiophenium Picrate*.—Chloroacetyl chloride (8 g) and thioanisole (4.2 g) were added with stirring to anhydrous aluminium chloride (9 g) in dichloromethane cooled in ice–water. The mixture was refluxed for 3 h, cooled, and extracted cautiously with ice-cold water (2 × 30 ml). The organic layer was dried, solvent removed *in vacuo*, and the residue recrystallised from methanol to give 4-*methylthiophenacyl chloride* as pale pink platelets (1.7 g), m.p. 75—77 °C. The aqueous layer was treated with an excess of aqueous picric acid and the precipitate recrystallised from acetonitrile–ether to give 1-*methyl*-3(2H)-*oxobenzo*[b]*thiophenium picrate* as yellow crystals (2.5 g), m.p. 143—146 °C.

1,5-*Dimethyl*-3(2H)-*oxobenzo*[b]*thiophenium Hexafluorophosphate*.—Chloroacetyl chloride (6 g) and methyl *p*-tolyl sulphide (3 g) were added to anhydrous aluminium chloride (6.8 g) in dichloromethane (50 ml) and refluxed 2 h. The mixture was poured into ice (100 g)–concentrated hydrochloric acid (5 ml). The aqueous layer was separated and the organic layer extracted with water (50 ml) and retained. The aqueous extract was treated with potassium hexafluorophosphate (7 g) in water (20 ml) and the precipitate recrystallised from acetonitrile–ether to give 1,5-*dimethyl*-3(2*H*)-*oxobenzo*[b]*thiophenium hexafluorophosphate* as colourless crystals (1.65 g), m.p. 172—174 °C. Treatment with diazomethane gave the corresponding 3-*methoxy-compound*, m.p. 165—170 °C (decomp.). The organic layer was dried, the solvent removed, and the residue recrystallised from light petroleum to give 5-methylbenzo[*b*]thiophen-3(2*H*)-one as colourless crystals (0.5 g), m.p. 100—101 °C (lit.,[39] 102 °C).

1,5-*Dimethyl*-3(2H)-*oxobenzo*[b]*thiophenium Perchlorate*.—5-Methylbenzo[*b*]thiophen-3(2*H*)-one (0.4 g) and silver perchlorate (0.51 g) in 1,2-dichloroethane (25 ml) were treated with methyl iodide (0.5 ml) and stirred for 60 h. The solution was filtered and the residue washed with acetonitrile. An excess of ether was added and the resulting solid recrystallised from acetonitrile–ether to give 1,5-*dimethyl*-3(2H)-*oxobenzo*[b]*thiophenium perchlorate* as colourless crystals (0.45 g), m.p. 191—194 °C. With diazomethane the corresponding 3-*methoxy-derivative* was obtained, m.p. 162—165 °C.

Procedure for Synthesis of Diazo-ketones.—The carboxylic acid (0.05 mol) was refluxed with thionyl chloride (25 ml) for 1 h, and excess of thionyl chloride removed *in vacuo* at *ca.* 70 °C. Dry toluene (25 ml) was added and removed *in vacuo* at *ca.* 70 °C. The residue, suspended in dry toluene (75 ml), was added to diazomethane (0.15 mol) in ether (250 ml) with stirring at 0 °C and left overnight at room temperature. The solvent was removed *in vacuo* at *ca.* 50 °C to give the crude diazo-ketone which was not purified further.

2(1H)-*Oxothienyl*[3,2,1-de]*thianthrenium Perchlorate* (30).—Crude 1-diazoacetylthianthren (29) (0.85 g) from 1-thianthrencarboxylic acid [40] in acetonitrile (20 ml) was treated with 60% perchloric acid (0.6 ml) with stirring. After decantation from a deposit, addition of an excess of ether precipitated the *perchlorate* (30), which was recrystallised from acetonitrile–ether as yellow microcrystals (0.7 g), m.p. 200—204 °C (decomp.); $\lambda_{max.}$ (MeOH) 211 (10^{-4} ε 4.92), 255 (infl.) (1.46), 282 (infl.) (0.83), and 326 nm (infl.) (0.54); $\nu_{max.}$ 1 735, 1 590w, 1 555w, 1 410, 1 280w, 1 260, 1 185w, 1 165w, and 1 150w cm^{-1}. It was unchanged on refluxing in acetonitrile for 12 h.

2-*Methoxythienyl*[3,2,1-de]*thianthrenium Perchlorate* (31).—The oxo-compound (30) (1.0 g) in acetontrile (5 ml) was treated with diazomethane (0.2 g) in ether (10 ml). After 2 h an excess of ether was added and the precipitate recrystallised from nitromethane–ether to give the *perchlorate* (31) as pale pink microcrystals (0.6 g), m.p. 203—207 °C (decomp.), $\lambda_{max.}$ (MeOH) 211 (10^{-4} ε 2.47), 266 (infl. (1.88), 250 (1.27), and 314 nm (0.25); $\nu_{max.}$ 3 130w, 1 580, 1 535, 1 310w, 1 260w, 1 220w, 1 175w, 1 095, and 1 065 cm^{-1}. This perchlorate (0.2 g) in methanol (5 ml) was

treated with bromine (0.2 g) and left for 16 h. An excess of ether was added and the precipitate recrystallised from nitromethane–ether to give 1-(2-*bromo*-1-*methoxyvinyl*)-5-*methoxythianthrenium perchlorate* (32) as pale yellow microcrystals (0.15 g), m.p. 109—112 °C; $\lambda_{max.}$ 212 (infl.) (1.81), 218 (infl.) (1.95), 223 (2.02), 242 (infl.) (1.43), 258 (0.98), and 305 nm (0.33); $\nu_{max.}$ 3 400 (br), 1 620w, 1 590w, 1 590w, 1 565w, 1 530w, 1 410, 1 325w, 1 275w, 1 220, 1 155, and 1 095 cm^{-1}.

2-*Methylbenzo*[b]*thiophen*-7-*carboxylic Acid*.—The 7-bromo-compound (17) (12 g) in methyl iodide (17 ml) was added dropwise to magnesium turnings (7.9 g) in dry ether (125 ml) so as to maintain a steady reflux. After addition was complete the mixture was refluxed for 30 min, cooled, poured on to an excess of freshly crushed solid carbon dioxide, and worked up in the usual way to give 2-*methylbenzo*[b]*thiophen*-7-*carboxylic acid* as colourless crystals from ethanol–water (8 g), m.p. 204—207 °C.

Reaction of 7-*Diazoacetyl*-2-*methylbenzo*[b]*thiophen with Perchloric Acid in Ether*.—60% Perchloric acid in water (2 ml) was added to the benzo[*b*]thiophen suspended in dry ether (25 ml) at 0 °C with stirring. A precipitate formed which was insoluble in acetonitrile and nitromethane. The filtrate was washed with water, dried, and the solvent removed. T.l.c. of the residue on silica using toluene–chloroform–ethyl acetate (9.5 : 9.5 : 1) as moving phase gave (*a*) at R_F 0.2, 7-hydroxyacetyl-2-methylbenzo[b]thiophen (100 mg); (*b*) at R_F 0.5, 7-ethoxyacetyl-2-methylbenzo-[*b*]thiophen (100 mg); (*c*) at R_F 0.7 an unidentified compound (50 mg). All three substances gave 2,4-dinitrophenylhydrazones which were recrystallised from acetone–chloroform: (*a*) 7-*hydroxyacetal*-2-*methylbenzo*[b]*thiophen dinitrophenylhydrazone*, red needles, m.p. 253—257 °C (decomp.); (*b*) orange crystals, m.p. 227—240 °C; (*c*) m.p. 219—226 °C.

2-*Methyl*-5-(2-*methylbenzo*[b]*thiophen*-7-*yl*)*oxazolium Perchlorate* (35).—The diazoketone from 2-methylbenzo[*b*]-thiophen-7-carboxylic acid (3 g) in acetonitrile (100 ml) was treated with 60% perchloric acid (7 ml). An excess of ether was added and the precipitate recrystallised from acetonitrile–ether to give *perchlorate* (35) as colourless crystals (1.5 g), m.p. 185—191 °C; $\lambda_{max.}$ (MeOH) 212 (infl.) (10^{-4} ε 1.14), 216 (infl.) (1.57), 223 (infl.) (2.20), 224 (3.50), 250 (3.66), 253 (infl.) (3.62), 293 (2.28), 304 (infl.) (1.89), 311 (infl.) (1.22), 319 (0.87), and 323 nm (0.31). This perchlorate (1.43 g) in chloroform (150 ml) was stirred with sodium carbonate (7 g) and anhydrous magnesium sulphate (7 g) for 2 h and filtered. Solvent removal gave the crude base (1.0 g), which could not be recrystallised from toluene–light petroleum or ethanol but sublimed at 110 °C and 0.07 mmHg to give 2-*methyl*-5-(2-*methylbenzo*[b]*thiophen*-7-*yl*)-*oxazole* as colourless crystals, m.p. 46—52 °C; $\lambda_{max.}$ (MeOH) 223 (10^{-4} ε 1.06), 235 (1.06), 254 (infl.) (1.10), 260 (1.31), and 330 nm (0.47).

Reaction of 4-*diazoacetyldibenzo*[b,d]*thiophen with Perchloric Acid*.—(*a*) The diazoacetyl compound (4 g) in acetonitrile (50 ml) was treated with 60% perchloric acid (2.5 ml) with stirring. An excess of ether was added and the precipitate recrystallised repeatedly from acetonitrile–ether to give 5-(*dibenzo*[b,d]*thiophen*-4-*yl*)-2-*methyloxazolium perchlorate* (36) as colourless crystals (1.5 g), m.p. 203—216 °C (decomp.); $\lambda_{max.}$ (MeOH) 215 (10^{-4} ε 2.33), 242 (4.25), 261 (3.26), 285 (2.07), 295 (infl.) (1.06), 326 (0.52), and 339 nm (0.68).

(*b*) The diazoketone (1 g) in acetonitrile (15 ml) was treated with 60% perchloric acid (0.7 ml) with stirring. The precipitate from addition of an excess of ether was shown by ^1H n.m.r. spectroscopy to be a *ca.* equimolar mixture of (36) and possibly (37). It was dissolved in acetonitrile (5 ml) and triethylamine (0.8 ml), and after 5 min water (100 ml) was added. The mixture was extracted with chloroform, and the extract dried, evaporated, and the residue dissolved in acetonitrile–chloroform. Addition of an excess of ether gave the perchlorate (37) as off-white crystals (0.2 g). The supernatant was evaporated to give 5-(4-dibenzo[*b*,*d*]-thienyl)oxazole which was converted into (36) (0.3 g) by perchloric acid (60%) and ether.

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REFERENCES

1 R. Zahradník, *Adv. Heterocyclic Chem.*, 1965, **5**, 1.
2 R. M. Acheson and D. R. Harrison, *Chem. Comm.*, 1969; *J. Chem. Soc.* (*C*), 1970, 1764, and references cited therein.
3 D. C. Eaton, Ph.D. Thesis, New York University, 1968.
4 H. Hedeweg and H. Hogeveen, *Tetrahedron Letters*, 1974, 75.
5 J. Cotruvo and I. Dejani, *Chem. Comm.*, 1971, 436.
6 R. M. Acheson, R. J. Prince, and J. D. Wallis, unpublished data.
7 R. J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A. E. A. Porter, *J.C.S. Chem. Comm.*, 1978, 83.
8 K. Clarke, R. M. Scrowston, and T. M. Sutton, *J.C.S. Perkin I*, 1973, 623.
9 E. Campaigne, A. Dinner, and M. Haseman, *J. Heterocyclic Chem.*, 1971, **8**, 755.
10 P. Demerseman, J. P. LeChiartier, C. Pène, A. Cherutin, and R. Royer, *Bull. Soc. chim. France*, 1965, 1473.
11 S. Nishimura, M. Nakamura, M. Suzuki, and E. Imoto, *J. Chem. Soc.* (*Japan*), 1962, **83**, 343.
12 R. P. Napier, H. A. Kaufman, R. P. Driscoll, L. A. Glick, C. C. Chu, and H. M. Foster, *J. Heterocyclic Chem.*, 1970, **7**, 393.
13 C. E. Olson and A. R. Bader, *Org. Synth.*, 1955, **35**, 95.
14 W. K. Anderson, E. J. LaVoie, and J. C. Bottaro, *J.C.S. Perkin I*, 1976, 1.
15 P. R. Hammond, *J. Chem. Soc.*, 1962, 1370.
16 L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edition, Pergamon, New York, 1969, p. 164.
17 H. Gilman and S. Gray, *J. Org. Chem.*, 1958, **23**, 1476.
18 E. Campaigne and A. Ashby, *J. Heterocyclic Chem.*, 1969, **6**, 517.
19 W. T. Flowers, G. Holt, and M. A. Hope, *J.C.S. Perkin I*, 1974, 1116.
20 C. D. Hurd and K. L. Kreutz, *J. Amer. Chem. Soc.*, 1950, **72**, 5543.
21 J. Sicé, *J. Amer. Chem. Soc.*, 1953, **75**, 3697.
22 S. Gronowitz, *Arkiv Kemi*, 1960, **16**, 363.
23 F. Krollpffeifer, K. L. Schneider, and A. Wissner, *Annalen*, 1950, **566**, 139.
24 R. Huisgen, H. König, G. Binsch, and H. J. Sturm, *Angew. Chem.*, 1961, **73**, 368.
25 R. Lakham and B. Ternai, *Adv. Heterocyclic Chem.*, 1974, **17**, 100.
26 F. Johnson and R. Madroñero, *Adv. Heterocyclic Chem.*, 1966, **6**, 95.
27 Belsteins 'Handbuch der Organische Chemie,' 4th edn., 1952, vol. 19, 231.
28 R. M. Acheson and D. F. Nisbet, *J. Chem. Soc.* (*C*), 1971, 3291.
29 M. W. Cooper, D.Phil. Thesis, Oxford University, 1977.
30 Socony Mobil Oil Co., Inc., *Neth. Appl.*, 6,511,447 (*Chem. Abs.*, 1966, **65**, 7143).
31 J. D. Bu'lock, G. N. Smith, and C. T. Bedford, *J. Chem. Soc.*, 1962, 1405.

[32] L. F. Fieser and R. G. Kennelly, *J. Amer. Chem. Soc.*, 1935, **57**, 1611.
[33] D. T. Drewry and R. M. Scrowston, *J. Chem. Soc.* (*C*), 1969, 2750.
[34] V. G. Bukharov and T. E. Poydnyakova, *Izvest. Akad. Nauk S.S.S.R., otdel Khim. Nauk*, 1961, 135 (*Chem. Abs.*, 1961, **55**, 17616).
[35] J. Attenburrow, A. F. B. Cameron, T. H. Chapman, R. M. Evans, B. A. Hems, A. B. Jansen, and T. Walker, *J. Chem. Soc.*, 1952, 1094.
[36] E. Jones and I. M. Moodie, *Org. Synth.*, 1970, **50**, 104.
[37] W. H. Cherry, W. Davis, B. C. Ennis, and Q. N. Porter, *Austral. J. Chem.*, 1967, **20**, 313.
[38] Y. Matsuki and Y. Adachi, *J. Chem. Soc.* (*Japan*), 1968, **89**, 192.
[39] K. Auwers and F. Arndt, *Ber.*, 1909, **42**, 537.
[40] H. Gilman and D. R. Swayampati, *J. Amer. Chem. Soc.*, 1956, **78**, 2163.