Reactions of 1*H*-2-Benzothiopyran 2-Oxides with Active Methylene Compounds: A Novel Ring Contraction of 1-Aryl Derivatives to Benzo[*c*]thiophenes. *X*-Ray Molecular Structure of 1-(2,2-Diacetylvinyl)-3-phenylbenzo[*c*]thiophene

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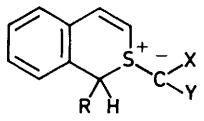
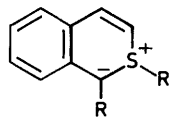
1-Aryl-1*H*-2-benzothiopyran 2-oxides (**5**) reacted with active methylene compounds in acetic anhydride to undergo a novel ring contraction, affording benzo[*c*]thiophene derivatives (**6**), whose structures have been established by *X*-ray crystallography of compound (**6a**). In contrast, 1-unsubstituted 1*H*-2-benzothiopyran 2-oxide (**1**), under the similar reaction conditions, afforded no benzothiophene derivatives, but instead gave 1-substituted 1*H*-2-benzothiopyrans (**2**) in good yield. It is proposed that the novel ring contraction was caused by the steric effects of the bulky aryl group at the 1-position of 2-benzothiopyran 2-oxides which prevent active methylene compounds from attacking at C-1.

In the course of our studies on sulphur ylide chemistry, we planned the preparation of stable exocyclic sulphur ylides (I) of 1*H*-2-benzothiopyran to compare their properties and chemical reactivities with those of stable endocyclic sulphur ylides (thianaphthalenes) (II), which we have extensively studied.[1–4]

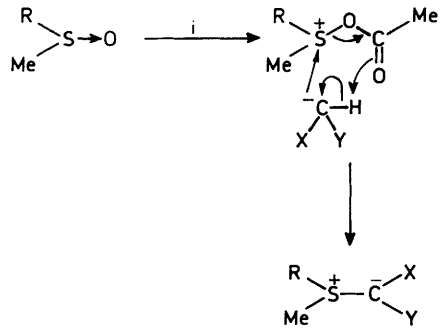


(I)



(II)

It is reported that the reaction of sulphoxides with active methylene compounds in acetic anhydride as a dehydrating agent afforded stable sulphur ylides *via* an acetoxysulphonium ion intermediate as shown in Scheme 1.[5–8]

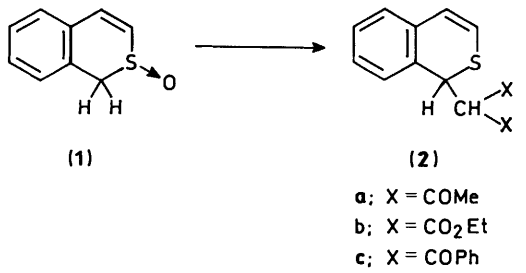


Scheme 1. *Reagents:* i, CH_2XY, Ac_2O

We now report that application of this sulphoxide–active methylene compound condensation method for the preparation of exocyclic sulphur ylides (I) resulted in unexpected ring contraction of the thiopyran ring in 2-benzothiopyran 2-oxides bearing an aryl group at the 1-position, and formation of 1-substituted 2-benzothiopyrans by attack of the active methylene compounds at C-1 of 1-unsubstituted 2-benzothiopyran 2-oxide.

Results and Discussion

1*H*-2-Benzothiopyran 2-oxide (**1**), prepared from the 1*H*-2-benzothiopyran[9] by *m*-chloroperbenzoic acid (MCPBA) oxidation, was allowed to react with an equimolar amount of acetylacetone in acetic anhydride at 100—110 °C to give 1-(diacetylmethyl)-1*H*-2-benzothiopyran (**2a**) in 80% yield, and no sulphur ylides were produced. The benzothiopyran (**2a**) was identified on the basis of elemental analysis as well as spectral evidence. Elemental analysis, and mass spectral data showing the molecular ion at *m/z* 246, indicate a molecular formula of $C_{14}H_{14}O_2S$ corresponding to structure (**2a**). The i.r. spectrum showed two characteristic absorption bands due to carbonyl groups at 1 720 and 1 700 cm^{-1}. In the ^1H n.m.r. spectrum (C_6D_6), the two acetyl groups appeared as two three-proton signals at δ 1.29 and 1.88, the methine hydrogen atom of the diacetylmethyl group as a one-proton doublet (*J* 11 Hz) at δ 4.30, the 1-H hydrogen as a one-proton double doublet (*J* 11 and 2 Hz) at δ 4.58, and olefinic hydrogen atoms as a one-proton double doublet (*J* 9 and 2 Hz) at δ 5.82 and a one-proton doublet (*J* 9 Hz) at δ 6.36. Analogous results were obtained by treating the sulphoxide (**1**) with equimolar amounts of diethyl malonate or dibenzoylmethane as active methylene compound, giving the corresponding 2-benzothiopyran, 1-bis(ethoxycarbonyl)methyl-(**2b**) or 1-dibenzoylmethyl-1*H*-2-benzothiopyran (**2c**) in 67 or 74% yield, respectively (Scheme 2). Elemental analyses and spectroscopic data were consistent with the structures (**2b**) and (**2c**). In particular, the ^1H n.m.r. spectra showed a characteristic one-proton double doublet due to 1-H

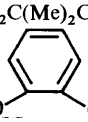


(1) (2)

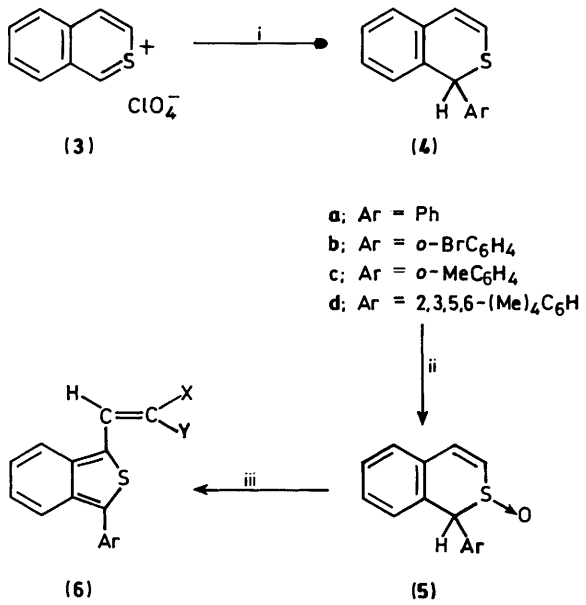
a; X = COMe
b; X = CO_2Et
c; X = COPh

Scheme 2. *Reagents:* CH_2X_2, Ac_2O

Table 1. Reactions of 1-aryl-1*H*-2-benzothiopyran 2-oxides (**5**) with active methylene compounds

Benzothiopyran 2-oxide	Ar	Product	X	Y	Yield (%)
(**5a**)	Ph	(**6a**)	COMe	COMe	16
		(**6b**)	COPh	COPh	10
		(**6c**)[a]	CN	CO_2Et	28
		(**6d**)[b]	COMe	CO_2Et	22
		(**6e**)	$-COCH_2C(Me)_2CH_2CO-$		10
		(**6f**)			19
(**5b**)	o-BrC_6H_4	(**6g**)	COMe	COMe	36
(**5c**)	o-MeC_6H_4	(**6h**)	COMe	COMe	51
(**5d**)	2,3,5,6-$(Me)_4C_6H$	(**6i**)	COMe	COMe	78
		(**6j**)	CO_2Et	CO_2Et	39

[a] As the sole isomer. [b] As an inseparable mixture of *E* and *Z* isomers.



Scheme 3. *Reagents:* i, ArMgBr; ii, MCPBA; iii, CH_2XY, Ac_2O

at δ 4.60 (*J* 11 and 3.8 Hz) for (**2b**) and at δ 5.08 (*J* 11 and 2 Hz) for (**2c**).

We next carried out the reaction of 1-aryl-substituted 2-benzothiopyran sulphoxides with active methylene compounds and found different results from those with 1-unsubstituted 2-benzothiopyran sulphoxides. The results are shown in Table 1. The required sulphoxides (**5**) were synthesized in good yield by MCPBA oxidation of the corresponding 1-aryl-2-benzothiopyrans (**4**) derived from Grignard reaction of 2-thianaphthylium perchlorate (**3**)[9] as shown in Scheme 3. These sulphoxides were isolated as the sole configurational isomer. The configuration is presumed to be *trans*, which results from the attack of MCPBA from the less hindered side, namely *anti* attack to the aryl group at 1-position.

Treatment of 1-phenyl-1*H*-2-benzothiopyran 2-oxide (**5a**) with a three-fold excess of acetylacetone under similar conditions as described for (**1**) afforded a complex mixture of products. Red crystals of compound (**6a**) were isolated as the main product in 16% yield (Table 1). The colour of the crystals suggested a high conjugated system for the structure. Elemental analysis, and mass spectral data exhibiting a molecular ion at *m/z* 320, indicate a molecular formula of $C_{20}H_{16}O_2S$. The i.r. spectrum showed absorption bands ascribable to the conjugated carbonyl groups at 1 690 and 1 640 cm^{-1}. In the u.v. spectrum, a strong absorption band at 453 nm (log ε 4.4) was observed. The ^1H n.m.r. spectrum, in addition to the six-proton singlet signal attributable to two acetyl groups at δ 2.53, showed a nine-proton multiplet at δ 7.10—7.91 and a one-proton singlet at δ 8.17. In the ^{13}C n.m.r. spectrum, except for the signals due to two methyl groups, each as a quartet (off-resonance) at δ 26.54 and 31.51, and two carbonyl groups at δ 196.36 and 204.86, all other signals appeared in the aromatic and olefinic regions. The foregoing evidence did not provide an exact structure for compound (**6a**). The structural determination of this molecule was finally carried out by *X*-ray analysis (see Experimental section for crystal data and other information). The molecular structure of compound (**6a**) is illustrated in the Figure.[10]

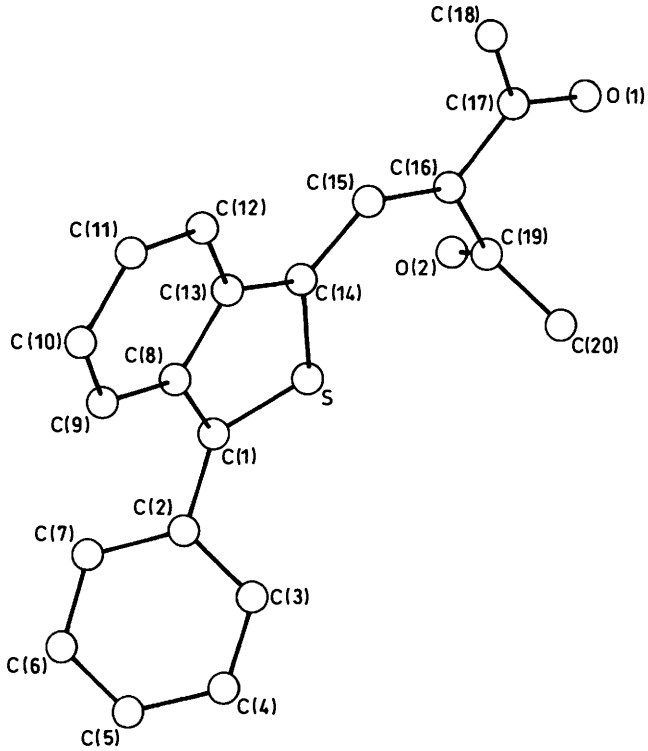
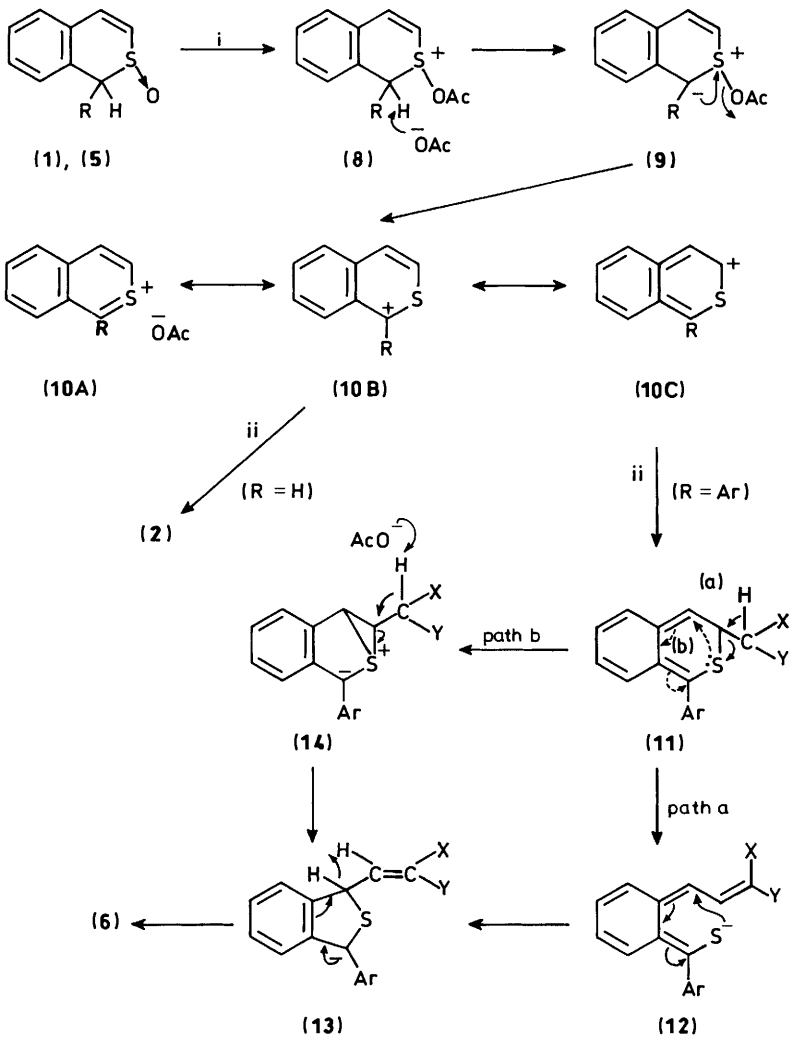
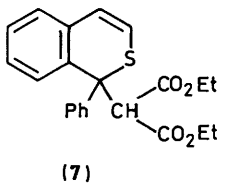


Figure. *X*-Ray molecular structure of 1-(2,2-diacetylvinyl)-3-phenylbenzo[*c*]thiophene (**6a**)



Scheme 4. *Reagents:* i, Ac_2O; ii, $\bar{C}HXY$



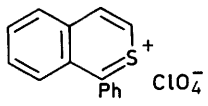
(7)

Clearly, these red crystals were of 1-(2,2-diacetylvinyl)-3-phenylbenzo[*c*]thiophene (**6a**). Other minor products, which could not be identified, and some polymeric materials were also obtained. The highly deshielded one-proton singlet at δ 8.17 in the ^{1}H n.m.r. spectrum is assignable to the olefinic proton of the substituent linked to benzo[*c*]thiophene. The reaction of the 2-benzothiopyran sulphoxide (**5a**) with other active methylene compounds, such as dibenzoylmethane, ethyl cyanoacetate, ethyl acetoacetate, dimedone, and indane-1,3-dione, under the same conditions as described above afforded the corresponding 3-phenyl-1-vinylbenzo[*c*]thiophene derivatives (**6b**—**f**) as red-coloured crystals in relatively low yield, together with other many unidentified products after preparative t.l.c. (p.l.c.) (Table 1). The structures of the benzothiophenes (**6b**—**f**) were fully supported by spectroscopic data and elemental analyses (see Experimental section). The ^{1}H n.m.r. spectra exhibited one-proton singlet signals characteristic of a highly deshielded olefinic hydrogen atom in the range δ 8.25—8.82. From the complex reaction mixture with dimedone, minor amounts of fairly purified pale yellow material, which was still contaminated with unidentified products, were isolated. The ^{1}H n.m.r. spectrum of the mixture appeared to indicate that the unknown had two acetyl groups and olefinic moiety and, moreover, the i.r. spectrum showed two strong carbonyl absorption bands at 1 700 and 1 658 cm^{-1}, thus possibly pointing to a ring-cleaved product of the 1-phenyl-1*H*-2-benzothiopyran ring by the attack of acetate ion.

The product distributions, as described above, are markedly influenced by the presence of the 1-phenyl substituent in the 2-benzothiopyran sulphoxides (**5a**). This observation is explicable in terms of the steric hindrance of the 1-phenyl group which plays an effective role in preventing active methylene compounds from attacking at C-1 of the 2-benzothiopyran ring. Reaction of diethyl malonate with 1-phenyl-2-benzothiopyran sulphoxide (**5a**), surprisingly, afforded no benzo[*c*]thiophene derivative, but a 54% yield of 1-bis(ethoxycarbonyl)methyl-1-phenyl-1*H*-2-benzothiopyran (**7**) after p.l.c., indicating that the reaction proceeded in the same fashion as for the sulphoxide (**1**).

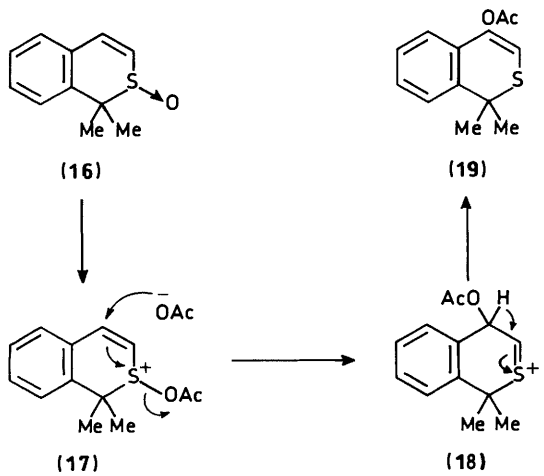
In considering the mechanism for this interesting reaction of 2-benzothiopyran sulphoxides and active methylene compounds, we propose the formation of 2-thianaphthylium cation (**10**) as a key intermediate as shown in Scheme. 4. When the acetoxysulphonium ion (**8**) was attacked by active methylene compounds, the exocyclic sulphur ylide might be formed by analogy with the open-chain sulphur ylides observed by Nozaki

et al.[5] The ionic intermediate (**8**), before being attacked by active methylene compounds, immediately undergoes deprotonation by acetate ion to give the intermediate (**10**), *via* acetoxysulphonium *ylide* (**9**), which corresponds to the normal Pummerer reaction intermediate, presumably because of the stability of (**10**) due to its aromaticity. In the case of (**10**; R = H), intermediate (**10B**), one of the resonance forms of (**10**), is attacked at the 1-position by active methylene compounds to give the products (**2**). In contrast, in the case where R = Ar, the attack of methylene compounds to C-1 is blocked by the bulky aryl group; consequently another resonance form (**10C**), less stable than (**10B**) but sterically opened at the 3-position, is attacked nucleophilically by active methylene compounds to afford intermediate (**11**), which undergoes ring contraction *via* intermediates (**12**) (path a) to form the intermediate (**13**). The intermediate (**13**) collapses to give the final products, benzo[*c*]thiophene derivatives (**6**). A reasonable alternative mechanism (path b) from (**11**) to (**13**) involves the intermediate (**14**). The similar intermediate to (**14**) was recently proposed for the thermal ring contraction of 2*H*-thiopyrans to thiophenes by Porter and co-workers.[11]



(**15**)

In order to get information pertaining to the 2-thianaphthylium cation intermediate, we treated 1-phenyl-2-thianaphthylium perchlorate (**15**) with acetylacetone under conditions similar to those of the reaction of 2-benzothiopyran sulphoxides to afford, as expected, the benzo[*c*]thiophene (**6a**) along with an unidentified complex mixture. 1,1-Dimethyl-1*H*-2-benzothiopyran 2-oxide (**16**), in which the formation of 2-thianaphthylium cation intermediate is suppressed by the two substituents at C-1, was treated with acetylacetone in acetic anhydride to give 4-acetoxy-1*H*-2-benzothiopyran (**19**) in 19% yield together with an undetermined complex mixture. It is interesting to note that the latter reaction did not give any exocyclic ylides in spite of the suppression of formation of 2-thianaphthylium cation, suggestive that there is no formation of sulphur ylide from this skeleton by acid anhydride-induced sulphoxide–active methylene compound condensation. The formation of 4-acetoxy compound (**19**) may be explained by the 1,4-addition of acetic anhydride to the sulphoxide (**16**), *via* intermediates (**17**) and (**18**), as depicted in Scheme 5.



(**16**) (**17**) (**18**) (**19**)

Scheme 5.

Note that the yields of the benzo[*c*]thiophenes are rather low, although the steric effects at the 1-position may play an effective role in controlling the reaction site. We assume one of the reasons for this low yield is a predominant attack of acetate ion at C-1 of the intermediate (**10B**), giving (tentatively) 1-acetoxy-1-phenyl-1*H*-2-benzothiopyran, which may probably undergo immediate decomposition under the reaction conditions to the ring-opened product we have isolated as a mixture from the reaction of the sulphoxide (**5**) and dimedone as described above. This assumption seems plausible because Nozaki *et al.*[5] reported that the principal side-reaction of the condensation of sulphoxides with active methylene compounds by means of acetic anhydride was the formation of thiols *via* the decomposition (hydrolysis) of α-acetoxy sulphides formed by Pummerer reaction, as first observed by Pummerer.[12] Such mechanistic considerations have motivated our investigation of the reaction of other 1*H*-2-benzothiopyran sulphoxides having a more bulky group at the 1-position, which is expected to prevent acetate ion from attacking C-1. Thus, we carried out the condensation of 1-(*o*-bromophenyl)-substituted sulphoxide (**5b**) with acetylacetone by means of acetic anhydride and obtained a 36% yield of the benzo[*c*]thiophene (**6g**) as red crystals. Furthermore, 1-(*o*-tolyl) derivative (**5c**) afforded a 51% yield of the corresponding benzo[*c*]thiophene (**6h**) as red crystals under the same reaction conditions. Finally, from the reaction of 1-(2,3,5,6-tetramethylphenyl)-substituted sulphoxide (**5d**) with acetylacetone, we obtained a 78% yield of the corresponding benzo[*c*]thiophene (**6i**). Interestingly, we could isolate, in 39% yield, the benzo[*c*]thiophene derivative (**6j**) as gold crystals from the sulphoxide (**5d**) and diethyl malonate, which did not afford any benzo[*c*]thiophene from the reaction with the 1-phenyl-substituted benzothiopyran (**5a**) as described above. These results are included in Table 1, and reveal that a bulky group at the 1-position of 2-benzothiopyrans prevents both active methylene compounds and acetate ion from attacking at C-1 position and accelerates the formation of benzo[*c*]thiophenes. The result that only diethyl malonate preferentially attacked at the 1-position of 1-phenyl-2-benzothiopyran ring is peculiar, because the steric hindrance of diethyl malonate is considered to be much more than that of ethyl cyanoacetate or ethyl acetoacetate, in the case of which benzo[*c*]thiophene derivative (**6c**) or (**6d**) was obtained in moderate yield as described above. In this case, the nucleophilicity of the enolate anions derived from active methylene compounds seems likely to determine the reaction site of 1-phenyl-2-thianaphthylium cation intermediate (**10**). The enolate anion formed from diethyl malonate is the most nucleophilic among those from the active methylene compounds we used in the present work, on the basis of their pK_a values (pK_a 13 for diethyl malonate, 9 for ethyl cyanoacetate and acetyl acetone, and 11 for ethyl acetoacetate[13]). The nucleophilicity of the enolate anion of diethyl malonate may be strong enough to overcome the steric hindrance of the 1-phenyl group and enable the anion to attack at C-1. However, the 2,3,5,6-tetraphenyl group in compound (**5d**) can prevent even a strong nucleophile from attacking at the 1-position because of its greater bulk.

In conclusion, we have developed a new synthetic method for the construction of highly conjugated benzo[*c*]thiophene derivatives *via* a novel ring contraction of 1-(bulky aryl group)-substituted 1*H*-2-benzothiopyran sulphoxides obtained from the condensation with active methylene compounds by means of acetic anhydride.

Experimental

M.p.s were measured on a Yanagimoto micro melting point apparatus, and are uncorrected. I.r. spectra were measured on a JASCO A-1 spectrophotometer. ^{1}H N.m.r. spectra were

recorded on Hitachi R-20B (60 MHz) or JEOL GX-270 (270 MHz) spectrometers using tetramethylsilane as internal standard. The chemical shifts are in δ-units (p.p.m.) with coupling constants in Hz. ^{13}C N.m.r. spectra were obtained using a JEOL GX-270 spectrometer. U.v. spectra were measured on a Hitachi Model 200–100 spectrophotometer. Mass spectra were obtained by using a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. Analytical and preparative t.l.c. were performed on E. M. Merck silica gel 60PF-254 plates. Light petroleum refers to the faction boiling in the range 35—60 °C.

1H-2-*Benzothiopyran* 2-*Oxide* (**1**).—MCPBA (85% purity; 2.33 g) was added to an ice-cooled solution of 1*H*-2-benzothiopyran[9] (1.7 g) in dichloromethane (130 ml), and the mixture was stirred for 17 h at room temperature, washed with aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated under reduced pressure. The residual oil was subjected to column chromatography on silica gel. The eluate with benzene afforded 1H-2-*benzothiopyran* 2,2-*dioxide* (210 mg), which was recrystallized from hexane–benzene as columns, m.p. 124—125 °C; $\nu_{max.}$ 1 290 and 1 110 cm^{-1} (SO_2); $\delta_H(CDCl_3)$ 4.42 (2 H, d, *J* 1 Hz, 1-H_2), 6.63 (1 H, dt, *J* 10.5 and 1 Hz, 3-H), 7.21 (1 H, d, *J* 10.5 Hz, 4-H), and 6.90—7.73 (4 H, m, ArH) (Found: C, 60.1; H, 4.5. $C_9H_8O_2S$ requires C, 60.0; H, 4.5%). The eluate with chloroform gave the *title sulphoxide* (1.46 g, 77.5%), which was recrystallized from benzene as columns, m.p. 149—150 °C; $\nu_{max.}$ 1 050 cm^{-1} (SO); $\delta_H(CDCl_3)$ 3.70 (1 H, d, *J* 17 Hz, 1-H), 6.50 (1 H, dd, *J* 17 and 1.5 Hz, 1-H), 6.92 (1 H, dd, *J* 10 and 1.5 Hz, 3-H), 7.23 (1 H, d, *J* 10 Hz, 4-H), and 7.42 (4 H, br s, ArH) (Found: C, 65.9; H, 4.8. C_9H_8OS requires C, 65.8; H, 4.9%).

Preparation of 1-*Aryl*-1H-2-*benzothiopyrans* (**4**).—1-*Phenyl*-1H-2-*benzothiopyran* (**4a**). Powdered 2-thianaphthylium perchlorate (**3**)[9] (10 g) was added in small portions to a stirred ethereal solution of phenylmagnesium bromide prepared from magnesium (3 g) and bromobenzene (19.3 g) in dry ether (100 ml) and the mixture was refluxed and stirred for 4 h. The reaction mixture was treated with aqueous NH_4Cl and the ether layer was separated, washed with water, dried ($MgSO_4$), and evaporated. The residual oil was purified by distillation to give the *title compound* (8.2 g, 90.3%) as an oil, b.p. 140 °C (0.1 mmHg); $\delta_H(CDCl_3)$ 5.11 (1 H, d, *J* 1.5 Hz, 1-H), 6.27 (1 H, dd, *J* 9.5 and 1.5 Hz, 3-H), 6.72 (1 H, d, *J* 9.5 Hz, 4-H), and 6.85—7.50 (9 H, m, ArH) (Found: C, 80.15; H, 5.6. $C_{15}H_{12}S$ requires C, 80.3; H, 5.4%).

The following compounds were prepared from the reaction of 2-thianaphthylium perchlorate (**3**) with the appropriate arylmagnesium bromide in a similar manner as above.

1-(o-*Bromophenyl*)-1H-2-*benzothiopyran* (**4b**), from *o*-bromophenylmagnesium bromide (36%), prisms, m.p. 81—82 °C (from light petroleum); $\delta_H(CDCl_3)$ 5.58 (1 H, d, *J* 1.5 Hz, 1-H), 6.23 (1 H, dd, *J* 10 and 1.5 Hz, 3-H), 6.77 (1 H, d, *J* 10 Hz, 4-H), and 6.74—7.83 (8 H, m, ArH) (Found: C, 59.2; H, 3.8. $C_{15}H_{11}BrS$ requires C, 59.4; H, 3.7%).

1-(o-*Tolyl*)-1H-2-*benzothiopyran* (**4c**), from *o*-tolylmagnesium bromide (85%), columns, m.p. 62—63 °C (from light petroleum); $\delta_H(CDCl_3)$ 2.47 (3 H, s, Me), 5.44 (1 H, s, 1-H), 6.31 (1 H, d, *J* 10 Hz, 3-H), 6.79 (1 H, d, *J* 10 Hz, 4-H), and 6.78—7.50 (8 H, m, ArH) (Found: C, 80.9; H, 6.0. $C_{16}H_{14}S$ requires C, 80.6; H, 5.9%).

1-(2,3,5,6-*Tetramethylphenyl*)-1H-2-*benzothiopyran* (**4d**), from 2,3,5,6-tetramethylphenylmagnesium bromide in tetrahydrofuran (32.2%) after column chromatography on silica gel [hexane–EtOAc (10:1)], prisms, m.p. 113—114 °C (from dichloromethane–hexane); $\delta_H(CDCl_3)$ 2.20 (3 H, s, Me), 2.24 (3 H, s, Me), 2.29 (3 H, s, Me), 2.34 (3 H, s, Me), 6.44 (1 H, d, *J* 10 Hz, 3-H), 6.44 (1 H, s, 1-H), 6.59 (1 H, d, *J* 10 Hz, 4-H), 6.66—6.69 (1 H, m, ArH), and 6.99—7.18 (4 H, m, ArH); $\delta_C(CDCl_3)$ 15.79 (q), 20.23 (q), 20.37 (q), 21.16 (q), 43.51 (d), 124.12 (d), 125.08 (d), 125.90 (d), 127.16 (d), 127.30 (d), 128.08 (d), 131.69 (d), 132.01 (s), 132.94 (s), 133.58 (s), 133.67 (s), 133.79 (s), 135.36 (s), and 135.85 (s); *m/z* 280 (M^+) (Found: C, 81.4; H, 7.25. $C_{19}H_2OS$ requires C, 81.4; H, 7.2%).

Preparation of 1-*Aryl*-1H-2-*benzothiopyran* 2-*Oxides* (**5**).—1-*Phenyl*-1H-2-*benzothiopyran* 2-*oxide* (**5a**). MCPBA (85% purity; 1.81 g) was added to a stirred and ice-cooled solution of compound (**4a**) (2 g) in dichloromethane (100 ml), and the mixture was stirred for 17 h at room temperature. After addition of saturated aqueous $NaHCO_3$, the organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated to give the *title compound* (1.82 g, 84.9%) as needles, m.p. 124 °C; $\nu_{max.}$ 1 030 cm^{-1} (SO); $\delta_H(CDCl_3)$ 5.61 (1 H, d, *J* 1.5 Hz, 1-H), 6.66 (1 H, dd, *J* 10 and 1.5 Hz, 3-H), and 6.95—7.55 (10 H, m, ArH and 4-H) (Found: C, 74.9; H, 5.0. $C_{15}H_{12}OS$ requires C, 75.0; H, 5.0%).

The following sulphoxides were prepared from the corresponding sulphides in a similar manner as above.

1-(o-*Bromophenyl*)-1H-2-*benzothiopyran* 2-*oxide* (**5b**) (91.3%), prisms, m.p. 162—164 °C (from hexane–CH_2Cl_2); $\nu_{max.}$ 1 030 cm^{-1} (SO); $\delta_H(CDCl_3)$ 6.05 (1 H, s, 1-H), 6.53—6.56 (1 H, m, ArH), 6.67 (1 H, *J* 9.8 Hz, 3-H), and 7.07—7.67 (8 H, m, ArH and 4-H); $\delta_C(CDCl_3)$ 65.56 (d), 123.18 (d), 126.43 (s), 127.74 (d), 129.01 (s), 129.23 (d), 129.87 (d), 130.08 (s), 131.17 (d), 131.82 (d), 133.56 (d), and 135.24 (d); *m/z* 318 (M^+) (Found: C, 56.2; H, 3.5. $C_{15}H_{11}BrOS$ requires C, 56.4; H, 3.5%).

1-(o-*Tolyl*)-1H-2-*benzothiopyran* 2-*oxide* (**5c**) (68.6%), needles, m.p. 150.5—154 °C (decomp.) (from hexane–CH_2Cl_2); $\nu_{max.}$ 1 022 cm^{-1} (SO); $\delta_H(CDCl_3)$ 2.68 (3 H, s, Me), 5.78 (1 H, s, 1-H), 6.43—6.75 (2 H, m, ArH and 3-H), and 6.80—7.40 (8 H, m, ArH and 4-H); $\delta_C(CDCl_3)$ 19.94 (q), 63.57 (d), 123.52 (d), 126.30 (d), 128.19 (d), 128.28 (d), 128.67 (s), 128.78 (d), 129.63 (d), 129.77 (s), 129.97 (s), 130.87 (d), 131.01 (d), 131.34 (d), 135.03 (d), and 137.89 (s); *m/z* 254 (M^+) (Found: C, 75.4; H, 5.5. $C_{16}H_{14}OS$ requires C, 75.6; H, 5.55%).

1-(2,3,5,6-*Tetramethylphenyl*)-1H-2-*benzothiopyran* 2-*oxide* (**5d**) (63.7%) after p.l.c. on silica gel [hexane–EtOAc (1 : 3)], prisms, m.p. 154—157 °C (decomp.) (from ether–CH_2Cl_2); $\nu_{max.}$ 1 030 cm^{-1} (SO); $\delta_H(CDCl_3)$ 2.01 (3 H, s, Me), 2.20 (3 H, s, Me), 2.31 (3 H, s, Me), 2.36 (3 H, s, Me), 6.52 (1 H, d, *J* 10.5 Hz, 3-H), 6.53 (1 H, s, 1-H), 6.73 (1 H, d, *J* 10.5 Hz, 4-H), 6.71 (1 H, d, *J* 7.8 Hz, ArH), and 7.03—7.26 (4 H, m, ArH); $\delta_C(CDCl_3)$ 16.68 (q), 19.43 (q), 20.26 (q), 21.16 (q), 67.23 (d), 127.03 (d), 128.27 (d), 129.38 (d), 130.08 (d), 130.34 (d), 130.72 (s), 131.54 (d), 131.85 (d), 132.55 (d), 132.73 (s), 133.51 (s), 134.24 (s), 135.68 (s), and 135.93 (s); *m/z* 296 (M^+) (Found: C, 76.6; H, 6.8. $C_{19}H_{20}OS$ requires C, 77.0; H, 6.8%).

1-*Substituted* 1H-2-*Benzothiopyrans* (**2**) *Derived from the Sulphoxide* (**1**) *and Active Methylene Compounds in Acetic Anhydride*. 1-*Diacetylmethyl*-1H-2-*benzothiopyran* (**2a**).—A mixture of the sulphoxide (**1**) (690 mg) and acetylacetone (420 mg) in acetic anhydride (12 g) was stirred for 20 h at 100—110 °C. The reaction mixture was diluted with 20% aqueous sodium hydroxide at 0 °C until the solution became basic (pH 10), and was then extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$), and evaporated to give the *title compound* (825 mg, 79.6%) as pale yellow needles after recrystallization from ether, m.p. 96—97 °C; $\nu_{max.}$ 1 720 and 1 700 cm^{-1} (CO); $\delta_H(C_6D_6)$ 1.29 (3 H, s, Me), 1.88 (3 H, s, Me), 4.30 (1 H, d, *J* 11 Hz, COCHCO), 4.58 (1 H, dd, *J* 11 and 2 Hz, 1-H), 5.82 (1 H, dd, *J* 9 and 2 Hz, 3-H), 6.36 (1 H, d, *J* 9 Hz, 4-H),

6.60—6.95 (3 H, m, ArH), and 7.10 (1 H, br s, ArH) (Found: C, 68.5; H, 5.6. $C_{14}H_{14}O_2S$ requires C, 68.3; H, 5.7%).

The following compounds were obtained from the sulphoxide (**1**) and appropriate active methylene compounds under similar conditions as above.

1-*Bis*(*ethoxycarbonyl*)*methyl*-1H-2-*benzothiopyran** (**2b**), from diethyl malonate (67%), prisms, m.p. 59—60 °C (from MeOH) after p.l.c. on silica gel with benzene–chloroform (2:1) as solvent; $\nu_{max.}$ 1 750 and 1 718 cm^{-1} (ester); $\delta_H(CDCl_3)$ 0.96 (3 H, t, *J* 7.5 Hz, CH_2Me), 1.30 (3 H, t, *J* 7.5 Hz, CH_2Me), 3.87 (2 H, q, *J* 7.5 Hz, CH_2Me), 4.01 (1 H, d, *J* 11 Hz, COCHCO), 4.28 (2 H, q, *J* 7.5 Hz, CH_2Me), 4.60 (1 H, dd, *J* 11 and 3.8 Hz, 1-H), 6.33 (1 H, dd, *J* 9.7 and 3.8 Hz, 3-H), 6.83 (1 H, d, *J* 9.7 Hz, 4-H), and 7.05—7.42 (4 H, m, ArH) (Found: C, 62.7; H, 5.8. $C_{16}H_{18}O_4S$ requires C, 62.7; H, 5.9%).

1-*Dibenzoylmethyl*-1H-2-*benzothiopyran* (**2c**), from dibenzoylmethane (73.7%), yellow needles, m.p. 146—147 °C (from MeOH–benzene); $\nu_{max.}$ 1 690 and 1 660 cm^{-1} (CO); $\delta_H(CDCl_3)$ 5.08 (1 H, dd, *J* 11 and 2 Hz, 1-H), 6.27 (1 H, d, *J* 11 Hz, COCHCO), 6.28 (1 H, dd, *J* 10 and 2 Hz, 3-H), 6.83 (1 H, d, *J* 10 Hz, 4-H), and 6.95—7.93 (14 H, m, ArH) (Found: C, 77.8; H, 4.8. $C_{24}H_{18}O_2S$ requires C, 77.8; H, 4.9%).

Benzo[c]*thiophenes* (**6**) *Derived from* 1-*Aryl*-1H-2-*benzothiopyran* 2-*oxides* (**5**) *and Active Methylene Compounds in Acetic Anhydride.* 1-(2,2-*Diacetylvinyl*)-3-*phenylbenzo*[c]*thiophene* (**6a**).—A mixture of the sulphoxide (**5a**) (1 g) and acetylacetone (1.26 g) in acetic anhydride (12 g) was heated and stirred at 100—110 °C for 11 h. The reaction mixture was diluted with 20% aqueous sodium hydroxide at 0 °C until the solution became basic, and was then extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$), and concentrated to dryness under reduced pressure to leave a red oil, which was subjected to p.l.c. on silica gel with light petroleum–ether (4:5) as solvent to give the *title compound* (214 mg, 16%). Recrystallization of this from ether afforded red prisms, m.p. 147—149 °C; $\nu_{max.}$ 1 690 and 1 640 cm^{-1} (CO); $\delta_H(CDCl_3)$ 2.53 (6 H, s, 2 × Me), 7.10—7.91 (9 H, m, ArH), and 8.17 (1 H, s, vinylic H); $\delta_C(CDCl_3)$ 26.54 (q), 31.51 (q), 119.29 (d), 121.94 (d), 124.58 (s), 125.30 (d), 126.92 (d), 129.10 (d), 129.18 (d), 129.41 (d), 130.75 (d), 132.86 (s), 134.81 (s), 142.99 (s), 145.83 (s), 196.31 (s), and 204.86 (s); $\lambda_{max.}$(EtOH) 210 (log ε 4.4), 228 (4.3), 279 (4.3), 315 (s, 3.9), and 453 nm (4.4); *m*/*z* 320 (M^+) (Found: C, 75.2; H, 5.0. $C_{20}H_{16}O_2S$ requires C, 75.0; H, 5.0%).

The following compounds were obtained from the reaction of 1-aryl-1*H*-2-benzothiopyran 2-oxides (**5**) with active methylene compounds in a similar manner as above.

1-(2,2-*Dibenzoylvinyl*)-3-*phenylbenzo*[c]*thiophene* (**6b**), from the sulphoxide (**5a**) and dibenzoylmethane (10%) after p.l.c. on silica gel [light petroleum–ether (3:2)], red prisms, m.p. 130—132 °C (from ether); $\nu_{max.}$ 1 670 and 1 620 cm^{-1} (CO); $\delta_H(CDCl_3)$ 7.00—8.00 (19 H, m, ArH) and 8.35 (1 H, s, vinylic H); *m*/*z* 444 (M^+) (Found: C, 81.1; H, 4.5. $C_{30}H_{20}O_2S$ requires C, 81.05; H, 4.5%).

1-(2-*Cyano*-2-*ethoxycarbonylvinyl*)-3-*phenylbenzo*[c]*thiophene*† (**6c**), from the sulphoxide (**5a**) and ethyl cyanoacetate (27.7%), red needles, m.p. 126—128 °C (from ether); $\nu_{max.}$ 2 210 (CN), and 1 705 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.40 (3 H, t, *J* 7 Hz, CH_2Me), 4.37 (2 H, q, *J* 7 Hz, CH_2Me), 7.10—8.05 (9 H, m, ArH), and 8.82 (1 H, s, vinylic H); $\delta_C(CDCl_3)$ 14.33 (q), 62.19 (t), 93.62 (s), 117.49 (s), 119.67 (d), 122.21 (d), 125.28 (s), 125.99 (d), 128.22 (d), 129.36 (d), 129.63 (d), 129.83 (d), 132.49 (s), 134.81 (s), 142.37 (d), 144.57 (s), 149.77 (s), and 163.90 (s); *m*/*z* 333 (M^+) (Found: C, 72.2; H, 4.4; N, 3.9. $C_{20}H_{15}NO_2S$ requires C, 72.05; H, 4.5; N, 4.2%).

1-(2-*Acetyl*-2-*ethoxycarbonylvinyl*)-3-*phenylbenzo*[c]*thiophene*‡ (**6d**) as an inseparable mixture (3:2) of *E* and *Z* isomers, from the sulphoxide (**5a**) and ethyl acetoacetate (21.8%), red needles, m.p. 134—136 °C (from ether); $\nu_{max.}$ 1 720 (ester) and 1 640 cm^{-1} (CO); $\delta_H(CDCl_3)$ of major isomer: 1.42 (3 H, t, *J* 7.3 Hz, CH_2Me), 2.48 (3 H, s, COMe), 4.48 (2 H, q, *J* 7.3 Hz, CH_2Me), 7.19—7.99 (m, ArH overlapped with ArH of minor isomer), and 8.49 (1 H, s, vinylic H); $\delta_H(CDCl_3)$ of minor isomer: 1.41 (3 H, t, *J* 7.3 Hz, CH_2Me), 2.59 (3 H, s, COMe), 4.37 (2 H, q, *J* 7.3 Hz, CH_2Me), 7.19—7.99 (m, ArH overlapped with ArH of major isomer), and 8.65 (1 H, s, vinylic H); $\delta_C(CDCl_3)$ of major isomer: 14.11 (q), 29.80 (q), 61.75 (t), 168.22 (s), and 194.39 (s); $\delta_C(CDCl_3)$ of minor isomer: 14.36 (q), 31.18 (q), 61.21 (t), 166.43 (s), and 200.91 (s); *m*/*z* 350 (M^+) (Found: C, 71.8; H, 5.2. $C_{21}H_{18}O_3S$ requires C, 72.0; H, 5.2%).

5,5-*Dimethyl*-2-[(3-*phenylbenzo*[c]*thiophen*-1-*yl*)*methylene*]*cyclohexane*-1,3-*dione* (**6e**), from the sulphoxide (**5a**) and dimedone (10%) after p.l.c. on silica gel [light petroleum–ether (1:1)], deep red prisms, m.p. 177—178.5 °C (from ether); $\nu_{max.}$ 1 670 and 1 622 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.13 (6 H, s, 2 × Me), 2.59 (4 H, s, 2 × CH_2), 7.13—8.13 (9 H, m, ArH), and 8.25 (1 H, s, vinylic H); *m*/*z* 345 (M^+) (Found: C, 76.8; H, 5.5. $C_{23}H_{20}O_2S$ requires C, 76.6; H, 5.6%).

1-(1,3-*Dioxoindan*-2-*ylidenemethyl*)-3-*phenylbenzo*[c]*thiophene* (**6f**), from the sulphoxide (**5a**) and indane-1,3-dione (19%), dark red needles, m.p. 244—247 °C (from CH_2Cl_2); $\nu_{max.}$ 1 710 and 1 670 cm^{-1} (CO); $\delta_H(CDCl_3)$ 7.27—8.28 (13 H, m, ArH) and 8.60 (1 H, s, vinylic H); *m*/*z* 366 (M^+) (Found: C, 78.6; H, 3.8. $C_{24}H_{14}O_2S$ requires C, 78.7; H, 3.8%).

3-(2-*Bromophenyl*)-1-(2,2-*diacetylvinyl*)*benzo*[c]*thiophene* (**6g**), from the sulphoxide (**5b**) and acetylacetone (35.7%) after p.l.c. on silica gel [light petroleum–ether (2:3)], red needles, m.p. 101—102.5 °C (from ether); $\nu_{max.}$ 1 690 and 1 640 cm^{-1} (CO); $\delta_H(CDCl_3)$ 2.49 (6 H, s, 2 × Me), 7.03—7.93 (8 H, m, ArH), and 8.21 (1 H, s, vinylic H); $\delta_C(CDCl_3)$ 26.41 (q), 31.29 (q), 118.96 (d), 122.12 (d), 124.12 (d), 124.92 (d), 125.37 (s), 126.67 (d), 127.29 (d), 130.58 (d), 132.83 (s), 132.96 (d), 133.32 (d), 135.13 (s), 136.40 (s), 141.53 (s), 142.61 (s), 196.30 (s), and 240.59 (s); *m*/*z* 398 (M^+) (Found: C, 59.9; H, 3.8. $C_{20}H_{15}BrO_2S$ requires C, 60.2; H, 3.8%).

1-(2,2-*Diacetylvinyl*)-3-(o-*tolyl*)*benzo*[c]*thiophene* (**6h**), from the sulphoxide (**5c**) and acetylacetone (50.7%) after p.l.c. on silica gel [hexane–EtOAc (3:1)], red oil; $\nu_{max.}$ 1 695 and 1 640 cm^{-1} (CO); $\delta_H(CDCl_3)$ 2.20 (6 H, s, 2 × COMe), 2.53 (3 H, s, Me), 7.12—7.37 (7 H, m, ArH), 7.90 (1 H, d, *J* 8.3 Hz, ArH), and 8.27 (1 H, s, vinylic H); $\delta_C(CDCl_3)$ 20.24 (q), 26.39 (q), 31.32 (q), 119.03 (d), 122.08 (d), 124.63 (s), 124.76 (d), 125.74 (d), 126.73 (d), 129.28 (d), 130.54 (d), 130.78 (d), 131.22 (s), 131.37 (d), 134.59 (s), 136.30 (s), 137.36 (d), 141.90 (s), 145.04 (s), 196.26 (s), and 204.64 (s); *m*/*z* 334 (M^+) (Found: M^+, 334.1006. $C_{21}H_{18}O_2$ requires *M*, 334.1008).

1-(2,2-*Diacetylvinyl*)-3-(2,3,5,6-*tetramethylphenyl*)*benzo*[c]*thiophene* (**6i**), from the sulphoxide (**5d**) and acetylacetone (77.7%) after p.l.c. on silica gel [hexane–ether (1:1)], red-brown prisms, m.p. 169—171 °C (from CH_2Cl_2–ether); $\nu_{max.}$ 1 658 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.85 (6 H, s, 2 × Me), 2.27 (6 H, s, 2 × Me), 2.53 (3 H, s, Me), 2.54 (3 H, s, Me), 7.08—7.16 (3 H, m, ArH), 7.26—7.36 (1 H, m, ArH), 7.91 (1 H, d, *J* 8.7 Hz, ArH), and 8.30 (1 H, s, vinylic H); $\delta_C(CDCl_3)$ 17.02 (q), 20.01 (q), 26.53 (q), 31.40 (q), 119.07 (d), 122.03 (d), 124.67 (d), 124.82 (s), 126.96 (d), 130.39 (s), 131.09 (d), 132.60 (d), 133.85 (s), 134.21 (s), 134.33 (s), 136.94 (s), 142.06 (s), 146.96 (s), 196.33 (s), and 204.74 (s); *m*/*z* 376 (M^+) (Found: C, 76.6; H, 6.5. $C_{24}H_{24}O_2S$ requires C, 76.6; H, 6.4%).

1-[2,2-*Bis*(*ethoxycarbonyl*)*vinyl*]-3-(2,3,5,6-*tetramethyl*-

* *Diethyl* (1H-2-*benzothiopyran*-1-*yl*)*malonate*.

† *Ethyl* 2-*cyano*-3-(3-*phenylbenzo*[c]*thiophen*-1-*yl*)*propenoate*.

‡ *Ethyl* 2-*acetyl*-3-(3-*phenylbenzo*[c]*thiophen*-1-*yl*)*propenoate*.

phenyl)benzo[c]*thiophene** (**6j**), from the sulphoxide (**5d**) and diethyl malonate (38.8%), gold leaflets, m.p. 179—181 °C (from hexane–CH_2Cl_2); $\nu_{max.}$ 1 725 and 1 715 cm^{-1} (ester); $\delta_H(CDCl_3)$ 1.35 (3 H, t, *J* 7.3 Hz, CH_2Me), 1.36 (3 H, t, *J* 7.3 Hz, CH_2Me), 1.86 (6 H, s, 2 × Me), 2.28 (6 H, s, 2 × Me), 4.34 (2 H, q, *J* 7.3 Hz, CH_2Me), 4.39 (2 H, q, *J* 7.3 Hz, CH_2Me), 7.06—7.10 (3 H, m, ArH), 7.23—7.31 (1 H, m, ArH), 7.91 (1 H, d, *J* 9.3 Hz, ArH), and 8.53 (1 H, s, vinylic H); $\delta_C(CDCl_3)$ 13.79 (q), 14.29 (q), 17.07 (q), 20.07 (q), 61.32 (t), 61.72 (t), 117.93 (s), 119.54 (d), 121.67 (d), 124.54 (d), 125.10 (s), 126.60 (d), 130.71 (s), 132.33 (d), 132.55 (d), 133.89 (d), 134.53 (s), 136.66 (s), 141.82 (s), 144.85 (s), 165.14 (s), and 167.12 (s); *m/z* 436 (M^+) (Found: C, 71.3; H, 6.4. $C_{26}H_{28}O_4S$ requires C, 71.5; H, 6.4%).

Reaction of the Sulphoxide (**5a**) *with Diethyl Malonate in Acetic Anhydride.*—A mixture of the sulphoxide (**5a**) (1 g) and diethyl malonate (2.02 g) in acetic anhydride (12 g) was heated and stirred at 100—110 °C for 11 h. Work-up as usual afforded 1-*bis(ethoxycarbonyl)methyl*-1-*phenyl*-1H-2-*benzothiopyran*† (**7**) (856 mg, 53.9%) after p.l.c. on silica gel [light petroleum–ether (3:2)]. Recrystallization of this from ethanol afforded pale yellow prisms, m.p. 104—105.5 °C; $\nu_{max.}$ 1 745 and 1 725 cm^{-1} (ester); $\delta_H(CDCl_3)$ 0.89 (3 H, t, *J* 7 Hz, CH_2Me), 1.17 (3 H, t, *J* 7 Hz, CH_2Me), 3.83 (2 H, q, *J* 7 Hz, CH_2Me), 4.10 (2 H, q, *J* 7 Hz, CH_2Me), 4.68 (1 H, s, COCHCO), 6.33 (1 H, d, *J* 10 Hz, 3-H), 6.67 (1 H, d, *J* 10 Hz, 4-H), and 6.80—7.76 (9 H, m, ArH) (Found: C, 69.1; H, 5.8. $C_{22}H_{22}O_4S$ requires C, 69.1; H, 5.8%).

1-*Phenyl*-2-*thianaphthylium Perchlorate* (**15**).—An ice-cooled solution of sulphuryl chloride (1.8 g), in dry ether (18 ml) was slowly added to an ice-cooled, stirred solution of the benzothiopyran (**4a**) (1.8 g) in dry ether (18 ml), and the mixture was stirred for 30 min. Ice-cooled dry ether (40 ml) was added and then ice-cooled 70% aqueous perchloric acid (18 ml) was slowly added. After being stirred for 3 h, the precipitates were collected and washed successively with dry ether, acetic acid, and dry ether. The dried crystals were recrystallized from acetic acid to give the *title compound* (1.6 g, 62%) as yellow needles, m.p. 183—184 °C (decomp.); $\nu_{max.}$ 1 090 cm^{-1} (ClO_4^-); $\delta_H(CF_3CO_2H)$ 7.99 (5 H, s, ArH), 8.15—8.80 (4 H, m, ArH), and 9.22 (2 H, s, ArH) (Found: C, 55.6; H, 3.5. $C_{15}H_{11}ClO_4S$ requires C, 55.8; H, 3.4%).

Reaction of the Perchlorate (**15**) *with Acetylacetone in Acetic Anhydride.*—The perchlorate (**15**) (1 g) was added to a stirred mixture of acetylacetone (310 mg), sodium acetate (254 mg), and acetic anhydride (11 g), and the mixture was heated and stirred at 90 °C for 11 h. Work-up as usual afforded a brown oil, which was submitted to p.l.c. on silica gel with light petroleum–ether (4:5) to give the benzo[*c*]thiophene derivative (**6a**) (70 mg, 7.1%). This was identified with the sample obtained from the sulphoxide (**5a**) and acetylacetone.

1,1-*Dimethyl*-1H-2-*benzothiopyran* 2-*Oxide* (**16**).—1-Methyl-2-thianaphthylium perchlorate[14] (1.45 g) was slowly added to a stirred, ethereal solution of methylmagnesium iodide prepared from magnesium (300 mg) and iodomethane (1.5 g) in dry ether at room temperature. The reaction mixture was hydrolysed with ice-cold aqueous ammonium chloride and extracted with ether. The extracts were dried ($MgSO_4$), and removal of the solvent under reduced pressure afforded 1,1-dimethyl-1*H*-2-benzothiopyran (950 mg, 96.5%) as a pale yellow oil; $\delta_H(CDCl_3)$ 1.62 (6 H, s, 2 × Me), 6.30 (1 H, d, *J* 9.8 Hz, 3-H), 6.70 (1 H, d, *J* 9.8 Hz, 4-H), and 7.00—7.30 (4 H, m, ArH). This oil was oxidized with MCPBA (1.08 g), as for oxidation of the sulphides (**4**), to give the *title compound* (860 mg, 83%), which was recrystallized from

* *Diethyl* [3-(2,3,5,6-*tetramethylphenyl*)*benzo*[c]*thiophen*-1-*yl*) *methylene*]*malonate*.

† *Diethyl* (1-*phenyl*-1H-2-*benzothiopyran*-1-*yl*)*malonate*.

Table 2. Final fractional co-ordinates (× 10^4) for non-hydrogen atoms in 1-(2,2-diacetylvinyl)-3-phenylbenzo[*c*]thiophene (**6a**). Estimated standard deviations are given in parentheses

Atom	*x*	*y*	*z*
S	3 713(1)	4 291(1)	1 617(1)
O(1)	5 353(5)	8 599(3)	6 403(3)
O(2)	2 224(4)	6 358(4)	4 385(3)
C(1)	4 261(5)	2 916(4)	251(4)
C(2)	3 083(5)	2 369(4)	−885(3)
C(3)	2 163(5)	3 317(4)	−1 159(4)
C(4)	1 110(6)	2 793(5)	−2 252(4)
C(5)	964(6)	1 332(5)	−3 052(4)
C(6)	1 849(5)	383(5)	−2 790(4)
C(7)	2 883(5)	882(4)	−1 698(4)
C(8)	5 865(5)	2 498(4)	385(4)
C(9)	6 830(5)	1 477(4)	−538(4)
C(10)	8 435(5)	1 299(4)	−249(4)
C(11)	9 190(5)	2 135(5)	1 008(4)
C(12)	8 307(5)	3 110(4)	1 920(4)
C(13)	6 630(5)	3 340(4)	1 641(4)
C(14)	5 585(5)	4 372(4)	2 423(4)
C(15)	6 071(5)	5 424(4)	3 693(4)
C(16)	5 290(5)	6 558(4)	4 492(4)
C(17)	6 137(6)	7 595(4)	5 728(4)
C(18)	7 891(6)	7 419(5)	6 083(4)
C(19)	3 592(5)	6 952(4)	4 205(4)
C(20)	3 644(6)	8 085(5)	3 698(5)

Table 3. Bond distances (Å) and angles (°) in 1-(2,2-diacetylvinyl)-3-phenylbenzo[*c*]thiophene (**6a**). Standard deviations are given in parentheses

Bond distances (Å)			
S–C(1)	1.711(4)	S–C(14)	1.726(4)
O(1)–C(17)	1.222(6)	O(2)–C(19)	1.220(5)
C(1)–C(2)	1.489(5)	C(1)–C(8)	1.398(5)
C(2)–C(3)	1.398(6)	C(2)–C(7)	1.405(6)
C(3)–C(4)	1.396(6)	C(4)–C(5)	1.380(7)
C(5)–C(6)	1.375(7)	C(6)–C(7)	1.389(6)
C(8)–C(9)	1.420(6)	C(8)–C(13)	1.449(5)
C(9)–C(10)	1.354(6)	C(10)–C(11)	1.446(6)
C(11)–C(12)	1.355(6)	C(12)–C(13)	1.422(5)
C(13)–C(14)	1.403(5)	C(14)–C(15)	1.445(5)
C(15)–C(16)	1.348(6)	C(16)–C(17)	1.496(6)
C(16)–C(19)	1.508(6)	C(17)–C(18)	1.488(7)
C(19)–C(20)	1.480(7)		
Bond angles (°)			
C(1)–S–C(14)	93.7(2)	S–C(1)–C(2)	119.3(3)
S–C(1)–C(8)	111.5(3)	C(2)–C(1)–C(8)	129.2(4)
C(1)–C(2)–C(3)	120.9(4)	C(1)–C(2)–C(7)	120.0(4)
C(3)–C(2)–C(7)	119.1(4)	C(2)–C(3)–C(4)	120.1(4)
C(3)–C(4)–C(5)	119.8(4)	C(4)–C(5)–C(6)	120.9(4)
C(5)–C(6)–C(7)	120.1(4)	C(2)–C(7)–C(6)	120.0(4)
C(1)–C(8)–C(9)	129.2(4)	C(1)–C(8)–C(13)	111.9(3)
C(9)–C(8)–C(13)	118.8(4)	C(8)–C(9)–C(10)	120.5(4)
C(9)–C(10)–C(11)	120.6(4)	C(10)–C(11)–C(12)	120.8(4)
C(11)–C(12)–C(13)	120.0(4)	C(8)–C(13)–C(12)	119.3(4)
C(8)–C(13)–C(14)	112.5(3)	C(12)–C(13)–C(14)	128.1(4)
S–C(14)–C(13)	110.5(3)	S–C(14)–C(15)	124.9(3)
C(13)–C(14)–C(15)	124.5(4)	C(14)–C(15)–C(16)	130.7(4)
C(15)–C(16)–C(17)	121.0(4)	C(15)–C(16)–C(19)	124.3(4)
C(17)–C(16)–C(19)	114.6(4)	O(1)–C(17)–C(16)	117.3(4)
O(1)–C(17)–C(18)	122.2(4)	C(16)–C(17)–C(18)	120.5(4)
O(2)–C(19)–C(16)	121.0(4)	O(2)–C(19)–C(20)	121.2(4)
C(16)–C(19)–C(20)	117.8(4)		

ether to afford needles, m.p. 91—93 °C; $\nu_{max.}$ 1 030 cm^{-1} (SO); $\delta_H(CDCl_3)$ 1.42 (3 H, s, Me), 1.90 (3 H, s, Me), 6.64 (1 H, d, *J* 10.2 Hz, 3-H), 7.00 (1 H, d, *J* 10.2 Hz, 4-H), and 7.18—7.66 (4 H, m, ArH) (*Found:* C, 68.8; H, 6.3. $C_{11}H_{12}OS$ requires C, 68.7; H, 6.3%).

Reaction of the Sulphoxide (**16**) *with Acetylacetone in Acetic Anhydride.*—A mixture of the sulphoxide (**16**) (500 mg) and acetylacetone (390 mg) in acetic anhydride (7.4 g) was stirred at 120 °C for 18 h. Work-up as usual afforded 4-*acetoxy*-1,1-*dimethyl*-1H-2-*benzothiopyran* (**19**) (115 mg, 19.4%), which was recrystallized from light petroleum to give needles, m.p. 127.5—128.5 °C; $\nu_{max.}$ 1 762 cm^{-1} (ester); $\delta_H(CDCl_3)$ 1.70 (6 H, s, 2 × Me), 2.26 (3 H, s, OCOMe), 6.10 (1 H, s, 3-H), and 7.15—7.35 (4 H, m, ArH); *m/z* 234 (M^+) (Found: C, 66.6; H, 5.95. $C_{13}H_{14}O_2S$ requires C, 66.7; H, 6.0%).

X-*Ray Study of* 1-(2,2-*Diacetylvinyl*)-3-*phenylbenzo*[c]*thiophene* (**6a**).—Red prismatic crystals were obtained from ether. A crystal 0.3 × 0.3 × 0.2 mm was used for *X*-ray study.

Crystal data. $C_{20}H_{16}O_2S$, M = 320.4, triclinic, space group $P\bar{1}$; a = 7.801(6), b = 10.121(7), c = 11.543(7) Å, α = 114.00(5), β = 88.68(6), γ = 96.68(6)°, V = 826.6 $Å^3$, $F(000)$ = 336, Z = 2, D_x = 1.29 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 2.0 cm^{-1}. The cell dimensions and intensities were measured on a Syntex R3 four-circle diffractometer with graphite-monochromated Mo-K_α radiation with ω-scan mode, to $2\theta_{max.}$ 45°. A total of 2 917 independent reflections were collected, of which 2 114 reflections [$I \geq 1.96\sigma(I)$] were stored as observed. The structure was solved by the heavy-atom method. All the hydrogen atoms except for those bonded to C(20) were found in a difference Fourier map. A block-diagonal least-squares method was applied in the refinement with anisotropic temperature factors for the non-hydrogen atoms and isotropic factors for the hydrogen atoms. The function minimized was $\Sigma w\Delta^2[\Delta = |F_o| - |F_c|; w = 1/\sigma^2(F_o)]$. The final R was 0.062, with $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.069$. Atomic scattering factors were taken from International Tables for *X*-ray Crystallography.[15] Data reduction and structure refinement were performed with Syntex XTL programs on a NOVA 3 computer. Final atomic parameters are given in Table 2, bond distances and angles in Table 3.*

* *Supplementary data.* see Instructions for Authors, section 5.6.3, in the January issue. Tables of the hydrogen atomic co-ordinates and the anisotropic thermal parameters are available on request from the Cambridge Crystallographic Data Centre.

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