Novel Conversions of Benzo[*b*]thiophen-3(2*H*)-ones into 1,2-Benzisothiazole and Tetrahydro-1,2-benzothiazepin-5-one Systems *via* Sulphimide Intermediates [1]

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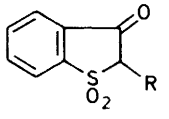
S-Amination of 2,2-dimethyl- (3a) and 2-benzyl-2-methyl-benzo[*b*]thiophen-3(2*H*)-one (3b) with *O*-mesitylenesulphonylhydroxylamine followed by treatment with base yielded 3-isopropenyl- (4a) and 3-(1-benzylvinyl)-1,2-benzisothiazole (4b), respectively. Similar treatment of 2-methyl-2-phenyl- (3c) and 2-methyl-2-(*p*-chlorophenyl)-benzo[*b*]thiophen-3(2*H*)-one (3d) gave, in addition to the corresponding 3-vinyl-1,2-benzisothiazoles (4c and d), 4-phenyl- (5a) and 4-(*p*-chlorophenyl)-2,3,4,5-tetrahydro-1,2-benzothiazepin-5-one (5b), respectively. Reaction of (3a) with chloramine-T gave the corresponding *N*-tosylsulphimide (9) and sulphoxide (10). Refluxng the *N*-tosylsulphimide (9) in benzene in the presence of triethylamine causes rearrangement to 4-methyl-2-tosyl-2,3,4,5-tetrahydro-1,2-benzothiazepin-5-one (12a). When the reaction of chloramine-T was applied to (3c), as many as four products, the corresponding 1,2-benzothiazepine (12b), one *N*-tosylsulphimide (15), and two isomeric sulphoxides (16) were isolated. Reaction pathways are discussed.

SULPHIMIDES have acquired considerable importance as reactive intermediates in organic synthesis in recent years.[2] In connection with our interest in the synthetic applications of sulphimides,[3] we now report novel transformations of benzo[*b*]thiophen-3(2*H*)-ones (3) to 3-vinyl-1,2-benzisothiazoles (4) [4] and tetrahydro-1,2-benzothiazepin-5-ones (5) and (12)† through sulphimide intermediates.

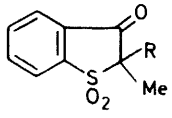
RESULTS AND DISCUSSION

The 2,2-disubstituted benzo[*b*]thiophen-3(2*H*)-ones (3a—d)‡ required in this study were synthesised by a three-step procedure from the benzo[*b*]thiophen-3(2*H*)-one 1,1-dioxides (1a—d). Thus, alkylation of (1a) with methyl iodide in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in benzene gave exclusively the 2,2-dimethyl derivative (2a) in 96% yield. Similarly, benzylation of (1b) with benzyl chloride and methylation of (1c,d) with methyl iodide gave the corresponding *C*-alkylated products (2b—d) in 91—100% yields. Reduction of (2a—d) with lithium aluminium hydride followed by oxidation with dimethyl sulphoxide–acetic anhydride gave the desired products (3a—d) in 42—74% yields.

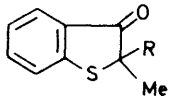
Benzo[*b*]thiophen-3(2*H*)-one (3a) was aminated with *O*-mesitylenesulphonylhydroxylamine (MSH) [7] in methylene chloride at room temperature. After evaporation of the solvent, the crude material [*S*-amine salt *i.e.* (6)] was directly treated with potassium carbonate in dimethylformamide at room temperature to give 3-isopropenyl-1,2-benzisothiazole (4a) in 82% yield. The structure of (4a) was based on its spectroscopic data. The u.v. spectrum of (4a) in ethanol showed absorption maxima at 224, 265sh, 308, and 317sh nm (log ε 4.04, 3.25, 3.54, and 3.50) which closely resembled that of (4e).[8,§] The n.m.r. spectrum of (4a) showed a methyl doublet at



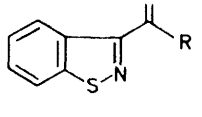
(1) a ; R = H
b ; R = Me
c ; R = Ph
d ; R = *p* − ClC$_6$H$_4$



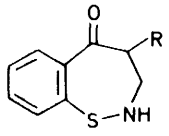
(2) a ; R = Me
b ; R = CH$_2$Ph
c ; R = Ph
d ; R = *p* − ClC$_6$H$_4$



(3) a ; R = Me
b ; R = CH$_2$Ph
c ; R = Ph
d ; R = *p* − ClC$_6$H$_4$



(4) a ; R = Me
b ; R = CH$_2$Ph
c ; R = Ph
d ; R = *p* − ClC$_6$H$_4$
e ; R = CH$_2$N(CH$_2$)$_2$O



(5) a ; R = Ph
b ; R = *p* − ClC$_6$H$_4$

δ 2.35 with *J* 1 Hz, a multiplet (2 H) between δ 5.5 and 5.7, and a multiplet (4 H) in the aromatic region (δ 8.3—

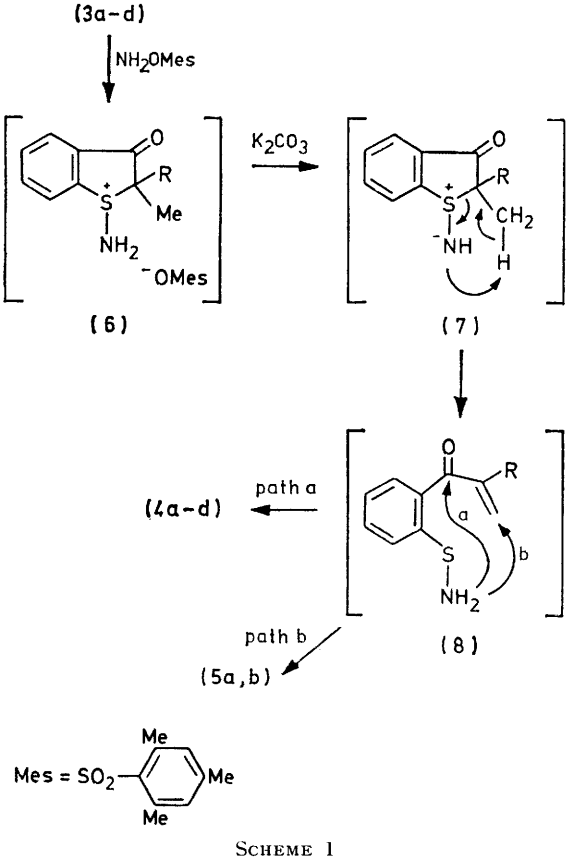
† The 1,2-benzothiazepine ring system has been known previously only as the 1,1-dioxide derivatives.[5]

‡ An alternative synthesis of (3c) involves a direct alkylation of 2-phenylbenzo[*b*]thiophen-3(2*H*)-one with methyl iodide but this gives both the *O*- and *C*-methylated derivatives in a *ca.* 1 : 1 ratio.[6]

§ Compound (4e) shows u.v. absorption maxima at 224, 264sh, 308, and 314sh nm (log ε 4.28, 3.43, 3.72, and 3.45). The authors are grateful to Drs. H. Uno and M. Kurokawa, Research Laboratories, Dainippon Pharmaceutical Co. Ltd., for sending a valuable sample of the oxalate of (4e).

7.3). Similarly, (3b) gave (4b) in 38% yield as the sole product. Interestingly, similar treatment of 2-phenyl derivative (3c) gave, in addition to (4c) (13%), a new product (38%) which was assigned the tetrahydro-1,2-benzothiazepin-5-one structure (5a) on the basis of spectroscopic evidence. The i.r. spectrum (KCl) of (5a) showed absorption bands at 3 310 (NH) and 1 665 (C=O) cm^{-1}. The n.m.r. spectrum of (5a) indicated a multiplet centred at δ 5.1 (1 H), a multiplet between δ 3.5—3.9 (2 H), and a broad signal at δ 3.2 (1 H, NH). The remaining signal was a multiplet (9 H) in the aromatic region (δ 7.8—7.1). Further support for the structure (5a) was obtained by tosylation to (12a) which will be described later. The 2-(*p*-chlorophenyl) derivative (3d) also gave two products, (4d) (18%) and (5b) (34%).

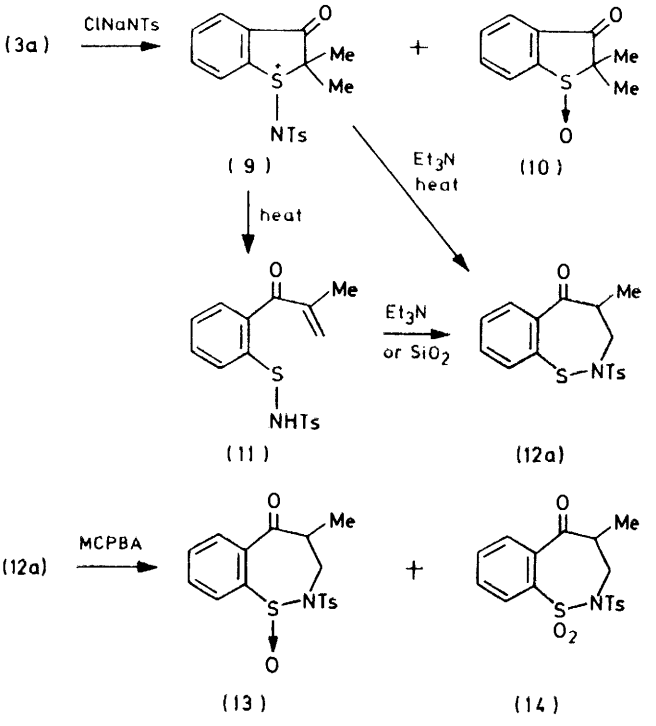
The formation of (4a—d) and (5a,b) can be rationalised in terms of the sulphenamide intermediates (8). The ring-opening may proceed *via* unisolable 'free' sulphimides (7) which undergo cycloelimination. The exclusive formation of (4b) provides good evidence for the cycloelimination mechanism which involves a five-membered cyclic transition state.[9] This requires *cis* stereochemistry of the $\overset{+}{S}$–$\overset{-}{N}$H and methyl group in the



Scheme 1

intermediate (7), which is that expected for the *S*-amination to the less hindered side of (3b) (opposite from the benzyl group) yielding material with the correct configuration. Intramolecular condensation of the sulphenamide group of the (8) thus formed with the carbonyl group (Scheme 1, path a) [10] may lead to the 1,2-benzisothiazoles (4). In the case of (3c,d) a Michael addition of the sulphenamide function to the enone system (path b) can compete with path a, leading to (5a) and (5b), perhaps due to steric hindrance to attack of the sulphenamide group to the carbonyl group by the bulky phenyl group and due to the electron-withdrawing property of the phenyl group.

We next investigated the behaviour of the corresponding *N*-tosylsulphimides. Reaction of (3a) with chloramine-T trihydrate in methanol containing a small amount of acetic acid gave the *N*-tosylsulphimide (9) and the sulphoxide (10) in 68 and 26% yields, respectively. Refluxing (9) in benzene in the presence of triethylamine

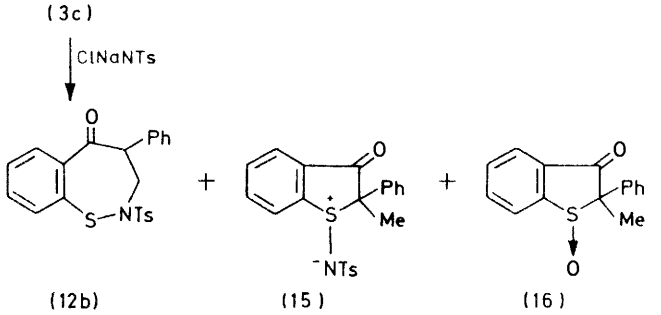


Scheme 2

afforded the tetrahydro-1,2-benzothiazepin-5-one (12a) in quantitative yield. The structure of (12a) was elucidated by its spectroscopic and chemical data. The i.r. spectrum showed a strong carbonyl absorption at 1 685 cm^{-1}. The n.m.r. spectrum did not exhibit the expected doublet for a 4-methyl group but a multiplet (centred at δ 1.22) was observed with the outer two signals of greater intensity than the inside ones. This type of splitting pattern is attributed to virtual coupling [11] arising from the fact that the chemical shifts of 3-H and 4-H are nearly identical (δ 3.6—4.0). This was supported by a europium shift reagent study: addition of $Eu(fod)_3$ caused separation of the signals of 3-H and 4-H, so that the 4-methyl signal appeared as a sharp doublet. Oxidation of (12a) with *m*-chloroperbenzoic acid (MCPBA) gave the sulphinamide (13) and the sulphonamide (14).

The transformation (9) ⟶ (12a) can be formulated as

proceeding by a cycloelimination followed by an intramolecular Michael addition of the resulting sulphenamide (11). In fact, refluxing (9) in benzene in the absence of base caused ring-opening to afford (11) as an oil, the structure of which was apparent from the n.m.r. spectrum, which showed a broad singlet at δ 2.02 (3 H, methyl), a singlet at δ 2.40 (3 H, toluene ring methyl), a broad signal at δ 5.15 (1 H, NH), and two broad signals at δ 5.45 and 5.78 (1 H each, vinylic protons). Treatment of (11) either with triethylamine in chloroform or with silicic acid in benzene at room temperature gave (12a) in quantitative yield.



SCHEME 3

When the reaction of chloramine-T was applied to the 2-methyl-2-phenyl derivative (3c), as many as four products, in addition to the starting material (37%), were isolated after preparative t.l.c.: the 1,2-benzothiazepine (12b) (30%), the *N*-tosylsulphenamide (15) (7%), and two isomeric sulphoxides (16) (9.3 and 2.3% yields). Since (12b) was not detected in the reaction mixture (on t.l.c.), and since only one isomer of the *N*-tosylsulphimide (15) was isolated, it is most likely that the predominantly formed *N*-tosylsulphimide (probably the isomer in which both the $\overset{+}{S}$–$\overset{-}{N}$Ts and 2-methyl groups are *cis* to each other) was converted into (12b) during work-up. In accordance with this view, the product ratio of (12b) and (15) was nearly identical to that of the isomeric sulphoxides (16).

EXPERIMENTAL

N.m.r. spectra were determined with a Hitachi R-22 spectrometer (90 MHz; tetramethylsilane as internal standard). I.r. spectra were recorded with a Hitachi EPI-G2 spectrophotometer and u.v. spectra with a Hitachi 124 spectrophotometer. Low- and high-resolution mass spectra were obtained with Hitachi RMU-6E and RMU-6M instruments with a direct inlet system, operating at 70 and 20 eV, respectively.

General Procedure for the Preparation of 2,2-*Disubstituted* 3-*Oxo*-2,3-*dihydrobenzo*[b]*thiophen* 1,1-*Dioxides* (2a—d).—A mixture of (1) (14 mmol), DBU (28—32 mmol), and methyl iodide (20—32 mmol) or benzyl chloride (21 mmol) in benzene (40 ml) was refluxed until the starting material disappeared (t.l.c.) (0.5—2.5 h). The precipitated solid was filtered off, and the benzene layer was washed with 10% hydrochloric acid and water, dried ($MgSO_4$), and concentrated. The residual solid was recrystallised from methanol. 2,2-*Dimethyl*-3-*oxo*-2,3-*dihydrobenzo*[b]*thiophen* 1,1-*dioxide* (2a) (96%) was obtained from (1a) [12] and methyl iodide, m.p. 84—85 °C (Found: C, 56.95; H, 4.75. $C_{10}H_{10}O_3S$ requires C, 57.12; H, 4.79%); $\nu_{max.}$ ($CHCl_3$) 1 720 (C=O), 1 305, and 1 165 (SO_2) cm^{-1}; δ ($CDCl_3$) 8.1—7.5 (4 H, m, aromatic) and 1.10 (6 H, s, 2 × 2-CH_3). 2-*Benzyl*-2-*methyl*-3-*oxo*-2,3-*dihydrobenzo*[b]*thiophen* 1,1-*dioxide* (2b) (91%) was obtained from (1b) [13] and benzyl chloride, m.p. 102—104 °C (Found: C, 66.9; H, 4.85. $C_{16}H_{14}O_3S$ requires C, 67.11; H, 4.92%); $\nu_{max.}$ ($CHCl_3$) 1 720 (C=O), 1 310, and 1 155 (SO_2) cm^{-1}; δ ($CDCl_3$) 8.1—7.1 (9 H, m, aromatic), 3.50 and 3.28 (1 H each, ABq, *J* 15 Hz, benzylic protons), and 1.50 (3 H, s, CH_3). 2-*Methyl*-2-*phenyl*-3-*oxo*-2,3-*dihydrobenzo*[b]*thiophen* 1,1-*dioxide* (2c) (98%) was obtained from (1c) [14] and methyl iodide, m.p. 159—160 °C (Found: C, 65.95; H, 4.35. $C_{15}H_{12}O_3S$ requires C, 66.15; H, 4.44%); $\nu_{max.}$ ($CHCl_3$) 1 720 (C=O), 1 320, and 1 160 (SO_2) cm^{-1}; δ ($CDCl_3$) 8.2—7.1 (9 H, m, aromatic) and 2.01 (3 H, s, 2-CH_3). 2-(p-*Chlorophenyl*)-2-*methyl*-3-*oxo*-2,3-*dihydrobenzo*[b]*thiophen* 1,1-*dioxide* (2d) (100%) was obtained from (1d) [14] and methyl iodide, m.p. 158—160 °C (Found: C, 58.45; H, 3.45. $C_{15}H_{11}ClO_3S$ requires C, 58.73; H, 3.61%); $\nu_{max.}$ ($CHCl_3$) 1 725 (C=O), 1 325, and 1 165 (SO_2) cm^{-1}; δ ($CDCl_3$) 8.2—7.0 (8 H, m, aromatic) and 2.00 (3 H, s, 2-CH_3).

General Procedure for the Preparation of 2,2-*Disubstituted Benzo*[b]*thiophen*-3(2H)-*ones* (3a—d).—To a rapidly stirred suspension of lithium aluminium hydride (1.56 g) in ether (30 ml) was added dropwise a solution of (3) (9 mmol) in ether–benzene (50 ml, 1 : 1 v/v), and the mixture was stirred at 25 °C for 5 h. The excess of hydride was hydrolysed with 10% hydrochloric acid and the organic layer was separated. The aqueous layer was extracted with benzene. The combined organic layer was washed with water, dried ($MgSO_4$), and concentrated to give an oily product which was passed through a column of short silica gel [n-hexane–benzene (2 : 1 v/v) as eluant] to give the 2,2-disubstituted 2,3-dihydrobenzo[*b*]thiophen-3-ol. The alcohol (4.7 mmol) was dissolved in acetic anhydride (7.5 ml) and dimethyl sulphoxide (10 ml). The mixture was stirred at room temperature for 18 h, poured into ice–water (100 ml), stirred for 3 h, and then extracted with n-hexane. The extract was washed with water several times, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel [n-hexane–benzene (10 : 1 v/v) as eluant] to give the pure product (3). 2,2-*Dimethylbenzo*[b]*thiophen*-3(2H)-one (3a) (60% overall yield) was an oil, $\nu_{max.}$ ($CHCl_3$) 1 675 (C=O) cm^{-1}; δ ($CDCl_3$) 7.8—6.95 (4 H, m, aromatic) and 1.58 (6 H, s, 2 × CH_3). It formed a 2,4-dinitrophenylhydrazone, m.p. 214—216 °C (from ethyl acetate) (Found: C, 53.6; H, 3.7; N, 15.6. $C_{16}H_{14}N_4O_4S$ requires C, 53.62; H, 3.93; N, 15.63%). 2-*Benzyl*-2-*methylbenzo*[b]*thiophen*-3(2H)-*one* (3b) (74%) was an oil; $\nu_{max.}$ ($CHCl_3$) 1 685 (C=O) cm^{-1}; δ ($CDCl_3$) 7.8—6.9 (9 H, m, aromatic), 3.08 (2 H, s, benzylic protons), and 1.54 (3 H, s, 2-CH_3). It formed a 2,4-dinitrophenylhydrazone, m.p. 173—175 °C (from ethanol) (Found: C, 60.6; H, 4.1; N, 12.65. $C_{22}H_{18}N_4O_4S$ requires C, 60.80; H, 4.17; N, 12.89%). 2-Methyl-2-phenylbenzo[*b*]thiophen-3(2*H*)-one (3c) (37%) had m.p. 95—97 °C (from propan-2-ol) (lit.,[6] 96–97 °C); $\nu_{max.}$ ($CHCl_3$) 1 690 (C=O) cm^{-1}; δ ($CDCl_3$) 7.9—7.0 (9 H, m, aromatic) and 2.00 (3 H, s, 2-CH_3). 2-(p-*Chlorophenyl*)-2-*methylbenzo*[b]*thiophen*-3(2H)-*one* (3d) (48%) had m.p. 66—68 °C (from methanol) (Found: C, 65.4; H, 3.95. $C_{15}H_{11}ClOS$ requires C, 65.56; H, 4.03%); $\nu_{max.}$ ($CHCl_3$) 1 700 (C=O) cm^{-1}; δ ($CDCl_3$) 7.8—7.0 (8 H, m, aromatic) and 1.94 (3 H, s, 2-CH_3).

3-*Isopropenyl*-1,2-*benzisothiazole* (4a).—To an ice-cooled solution of (3a) (110 mg, 0.6 mmol) in methylene chloride (5 ml) was added MSH (250 mg, 1.2 mmol) in methylene chloride (2 ml). The mixture was stirred at room temperature overnight and concentrated. The oily residue was dissolved in dimethylformamide (3 ml) and potassium carbonate (500 mg) was added. The mixture was stirred at room temperature for 30 min, poured into water (50 ml), and extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel [n-hexane–benzene (2 : 1 v/v) as eluant] to give (4a) as an *oil* (71 mg, 82%) (Found: M^+, 175.0435. $C_{10}H_9NS$ requires M, 175.0456).

3-(1-*Benzylvinyl*)-1,2-*benzisothiazole* (4b).—Using a similar procedure to that described above, (4b) (70 mg, 38%) and unchanged starting material (3b) (38 mg) were obtained from (3b) (190 mg). Compound (4b) was an *oil* (Found: M^+, 251.0766. $C_{16}H_{13}NS$ requires M, 251.0767); $\lambda_{max.}$ (EtOH) 224, 262sh, 307, and 316 nm (log ε 4.34, 3.63, 3.83, and 3.81); δ ($CDCl_3$) 8.2—6.8 (9 H, m, aromatic), 5.67 (1 H, s, $=CH_2$), 5.44 (1 H, d, J 2 Hz, $=CH_2$), and 4.07 (2 H, s, CH_2Ph).

3-(1-*Phenylvinyl*)-1,2-*benzisothiazole* (4c) *and* 4-*Phenyl*-2,3-*dihydro*-1,2-*benzothiazepin*-5(4H)-*one* (5a).—Using a similar procedure to that described above for the preparation of (4a), (5a) (194 mg, 38%) and an inseparable mixture (126 mg) of (4c) and the starting material (3c) were obtained from (3c) (0.48 g). The *benzothiazepinone* (5a) had m.p. 96—98 °C (from methanol) (Found: C, 70.5; H, 5.1; N, 5.55. $C_{15}H_{13}NOS$ requires C, 70.56; H, 5.13; N, 5.48%); *m/e* 255 (M^+). The mixture of (4c) and (3c) was treated with sodium borohydride (20 mg) in ethanol (5 ml) and then separated by preparative t.l.c. on silica gel (benzene as eluant) to give (4c) (60 mg, 13%) and an alcohol (54 mg). Compound (4c) was an *oil* (Found: M^+, 237.0616. $C_{15}H_{11}NS$ requires M, 237.0612); $\lambda_{max.}$ (EtOH) 219, 255sh, and 306 nm (log ε 3.87, 3,43, and 3.18); δ ($CDCl_3$) 8.0—7.0 (9 H, m, aromatic), 5.90 (1 H, d, J 2 Hz, $=CH_2$), and 5.71 (1 H, d, J 2 Hz, $=CH_2$).

3-(1-p-*Chlorophenylvinyl*)-1,2-*benzisothiazole* (4d) *and* 4-(p-*Chlorophenyl*)-2,3-*dihydro*-1,2-*benzothiazepin*-5(4H)-*one* (5b).—Using a similar procedure to that described for the preparation of (4c) and (5a), (5b) (72 mg, 34%) and an inseparable mixture (60 mg) of (4d) and unchanged (3d) were obtained from (3d) (200 mg). Compound (5b) had m.p. 123—125 °C (from methanol) (Found: C, 61.95; H, 4.05; N, 4.9. $C_{15}H_{12}ClNOS$ requires C, 62.17; H, 4.17; N, 4.83%); $\nu_{max.}$ ($CHCl_3$) 3 360 (NH) and 1 680 (C=O) cm^{-1}; δ ($CDCl_3$) 7.8—7.0 (8 H, m, aromatic), 5.00 (1 H, dd, J 8 and 9 Hz, 4-H), 3.8—3.1 (3 H, m, NH, and 3-H); *m/e* 284 (M^+). A mixture of (4d) and (3d) was treated with sodium borohydride (10 mg) in ethanol (5 ml) and the crude material was submitted to preparative t.l.c. on silica gel (benzene as eluant) to give a pure sample of (4d) (36 mg, 18%) and an oily alcohol (19 mg). The *isothiazole* (4d) had m.p. 105—106 °C (from methanol) (Found: C, 66.05; H, 3.6; N, 5.0. $C_{15}H_{10}ClNS$ requires C, 66.30; H, 3.70; N, 5.15%); $\lambda_{max.}$ (EtOH) 221, 242sh, 255sh, and 310 nm (log ε 4.36, 4.24, 4.10, and 3.72); δ ($CDCl_3$) 8.1—7.1 (8 H, m, aromatic), 5.92 (1 H, d, J 2 Hz, $=CH_2$), and 5.74 (1 H, d, J 2 Hz, $=CH_2$); *m/e* 271 (M^+).

Reaction of (3a) *with Chloramine-T*.—To a stirred solution of (3a) (1.6 g, 8.9 mmol) in methanol (20 ml) containing acetic acid (0.1 ml) was added chloramine-T trihydrate (2.78 g) in methanol (20 ml) at 0 °C. The mixture was sitrred for 50 min during which time the temperature was allowed to increase to room temperature. The solvent was evaporated *in vacuo* at low temperature and the residue was diluted with water and extracted with chloroform. The extract was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. The residue was dissolved in a mixture of methanol and ether and cooled to give crystalline 2,2-*dimethyl*-1-p-*tolylsulphonyliminobenzo*[b]*thiophen*-3(2H)-*one* (9) (1.72 g). The mother-liquor was concentrated and the residue was chromatographed on silica gel. Elution with benzene–ethyl acetate (1 : 1 v/v) to give further (9) (0.39 g, total yield 68%), m.p. 132—133 °C (from methanol) (Found: C, 58.7; H, 4.8; N, 4.15. $C_{17}H_{17}NO_3S$ requires C, 58.76; H, 4.93; N, 4.03%); $\nu_{max.}$ ($CHCl_3$) 1 720 (C=O), 1 290, 1 145, and 1 095 (SO_2), and 960 ($\overset{+}{S}-\overset{-}{N}$); δ ($CDCl_3$) 8.0—7.1 (8 H, m, aromatic), 2.43 (3 H, s, toluene ring CH_3), 1.63 (3 H, s, 2-CH_3), and 1.51 (3 H, s, 2-CH_3); *m/e* 347 (M^+). Further elution with benzene–ethyl acetate (1 : 4 v/v) gave 2,2-*dimethyl*-3-*oxo*-2,3-*dihydrobenzo*[b]*thiophen S-oxide* (10) (0.45 g, 26%), m.p. 49—51 °C (from benzene–n-hexane) (Found: C, 61.65; H, 5.1. $C_{10}H_{10}O_2S$ requires C, 61.83; H, 5.19%); $\nu_{max.}$ ($CHCl_3$) 1 700 (C=O) and 1 040 (S→O) cm^{-1}; δ ($CDCl_3$) 8.15—7.6 (4 H, m, aromatic), 1.60 (3 H, m, 2-CH_3), and 1.50 (3 H, s, 2-CH_3).

4-*Methyl*-2-p-*tolylsulphonyl*-2,3-*dihydro*-1,2-*benzothiazepin*-5(4H)-*one* (12a).—(*a*) A solution of (9) (150 mg) in benzene (6 ml) was refluxed for 1 h and concentrated *in vacuo* to give crude (11) (150 mg) as an oil, $\nu_{max.}$ ($CHCl_3$) 1 630 (C=O), 1 605 (C=C), 1 335, and 1 125 (SO_2) cm^{-1}. To a solution of (11) (150 mg) in benzene (6 ml) was added silicic acid (300 mg) and the mixture was stirred at room temperature for 2 h and filtered. The filtrate was concentrated and the residue was passed through a short column of silica gel [benzene–ethyl acetate (10 : 1 v/v) as eluant] to give the *benzothiazepinone* (12a) (130 mg, 87%), m.p. 102—103 °C (from methanol) (Found: C, 58.65; H, 4.85; N, 4.05. $C_{17}H_{17}NO_3S_2$ requires C, 58.76; H, 4.93; N, 4.03%); $\nu_{max.}$ ($CHCl_3$) 1 685 (C=O), 1 360, and 1 165 (SO_2) cm^{-1}; δ ($CDCl_3$) 7.6—6.8 (8 H, m, aromatic), 4.0—3.6 (3 H, m, 3- and 4-H), 2.24 (3 H, s, toluene ring CH_3), and 1.2—1.15 (3 H, m, 4-CH_3) [addition of $Eu(fod)_3$ (25 mg) caused one of 3-H to appear as a triplet (J 12 Hz), 4-H as a broad sextet, the other 3-H as a four-line signal, and 4-methyl as a sharp doublet (J 6 Hz)].

(*b*) A solution of (11) (150 mg) in chloroform (5 ml) containing triethylamine (0.02 ml) was stirred at room temperature for 1 h. The mixture was washed with 10% hydrochloric acid and water, dried ($MgSO_4$), and concentrated to give (12a) (150 mg, 100%).

(*c*) A solution of (9) (100 mg, 0.29 mmol) in benzene (10 ml) containing triethylamine (0.02 ml) was refluxed for 1.5 h. Work-up as described above gave (12a) (100 mg, 100%).

4-*Methyl*-5-*oxo*-2-p-*tolylsulphonyl*-2,3,4,5-*tetrahydro*-1,2-*benzothiazepine* 1-*Oxide* (13) *and* 1,1-*Dioxide* (14).—To an ice-cooled solution of (12a) (215 mg, 0.62 mmol) in chloroform (10 ml) was added MCPBA (255 mg, 1.47 mmol) portionwise and the mixture was stirred at room temperature for 24 h. The mixture was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. The crude material was chromatographed on silica gel. Elution with benzene–ethyl acetate (20 : 1 v/v) gave the *dioxide* (14) (130 mg, 56%), m.p. 130—132 °C (from methanol) (Found: C, 53.45; H, 4.45; N, 3.7. $C_{17}H_{17}NO_5S_2$ requires C, 53.81; H, 4.51; N, 3.69%); $\nu_{max.}$ ($CHCl_3$) 1 695 (C=O), 1 380, and 1 165 (SO_2) cm^{-1}; δ ($CDCl_3$) 8.1—7.2 (8 H, m, aromatic), 4.12 (2 H, d, J 8 Hz, 3-H), 3.48 (1 H, sextet, J 8 Hz, 4-H),

2.44 (3 H, s, toluene ring CH_3), and 1.24 (3 H, d, *J* 8 Hz, 4-CH_3); *m/e* 379 (M^+). Further elution with the same solvent gave the *oxide* (13) (66 mg, 30%), m.p. 196—198 °C (from methanol) (Found: C, 55.65; H, 4.65; N, 3.85. $C_{17}H_{17}NO_4S_2$: C, 56.18; H, 4.71; N, 3.85%); $\nu_{max.}$ ($CHCl_3$) 1 695 (C=O), 1 365, 1 165 (SO_2), and 1 095 (S→O) cm^{-1}; δ ($CDCl_3$) 8.1—7.3 (8 H, m, aromatic), 3.9—3.2 (3 H, m, 3-H and 4-H), 2.46 (3 H, s, toluene ring CH_3), and 1.2—1.05 (3 H, m, 4-CH_3); *m/e* 363 (M^+).

4-*Phenyl*-2-p-*tolylsulphonyl*-2,3-*dihydro*-1,2-*benzothiazepin*-5(4H)-*one* (12b).—(a) *From* (3c). To a stirred solution of (3c) (300 mg, 1.25 mmol) in methanol (10 ml), methylene chloride (5 ml), and acetic acid (0.01 ml) was added chloramine-T trihydrate (351 mg, 1.26 mmol) at 0 °C. The mixture was stirred at the same temperature for 2.5 h and concentrated *in vacuo* at low temperature. The residue was dissolved in chloroform and the solution was washed with 5% sodium hydroxide and water, dried ($MgSO_4$), and concentrated. The oily residue was submitted to preparative t.l.c. on silica gel (benzene as eluant) to give starting material (3c) (111 mg, 37%), (12b) (152 mg, 30%), and a mixture of (15) and (16). The *thiazepinone* (12b) had m.p. 138—140 °C (from methanol) (Found: C, 64.4; H, 4.6; N, 3.5. $C_{22}H_{19}NO_3S_2$ requires C, 64.5; H, 4.65; N, 3.4%); $\nu_{max.}$ (KCl) 1 675 (C=O), 1 350, and 1 165 (SO_2); δ ($CDCl_3$) 7.6—6.9 (13 H, m, aromatic), 5.04 (1 H, dd, *J* 12 and 6 Hz, 4-H), 4.62 (1 H, t, *J* 12 Hz, 3-H), 3.84 (1 H, dd, *J* 12 and 6 Hz, 3-H), and 2.24 (3 H, s, toluene ring CH_3); *m/e* 409 (M^+). The mixture of (15) and (16) was resubjected to preparative t.l.c. [benzene–ethyl acetate (9 : 1 v/v) as eluant] to give (15) (33 mg, 7%), and two isomeric sulphoxides (16) (30 mg, 9.3% and 7.5 mg, 2.3%). 2-*Methyl*-2-*phenyl*-1-p-*tolylsulphonyliminobenzo*[b]*thiophen*-3(2H)-*one* (15) had m.p. 162—163 °C (from methanol) (Found: C, 64.45; H, 4.55; N, 3.45. $C_{22}H_{19}NO_3S_2$ requires C, 64.52; H, 4.67; N, 3.42%); $\nu_{max.}$ ($CHCl_3$) 1 720 (C=O), 1 290, 1 145, 1 090 (SO_2), and 950 ($\overset{+}{S}-\overset{-}{N}$); δ ($CDCl_3$) 8.2—6.9 (13 H, m, aromatic), 2.40 (3 H, s, toluene ring CH_3), and 2.10 (3 H, s, 2-CH_3); *m/e* 409 (M^+). The major isomer of 2-*methyl*-3-*oxo*-2-*phenyl*-2,3-*dihydrobenzo*[b]*thiophen* S-*oxide* (16) had m.p. 117—119 °C [from ethyl acetate–light petroleum (b.p. 40—60 °C)] (Found: C, 70.35; H, 4.65. $C_{15}H_{12}O_2S$ requires C, 70.28; H, 4.72%); $\nu_{max.}$ ($CHCl_3$) 1 700 (C=O) and 1 035 (S→O) cm-1; δ ($CDCl_3$) 8.2—7.1 (9 H, aromatic) and 1.92 (3 H, s, CH_3); *m/e* 256 (M^+). The minor isomer of (16) had m.p. 129—130 °C [from ethyl acetate–light petroleum (b.p. 40—60 °C)] (Found: C, 70.15; H, 4.55); $\nu_{max.}$ ($CHCl_3$) 1 700 (C=O) and 1 040 (S→O) cm^{-1}; δ ($CDCl_3$) 8.2—7.1 (9 H, m, aromatic) and 1.99 (3 H, s, 2-CH_3); *m/e* 256 (M^+).

(b) *From* (5a). A solution of (5a) (50 mg, 0.19 mmol) and tosyl chloride (39 mg, 0.20 mmol) in pyridine (0.5 ml) was kept at room temperature overnight, poured into water containing 10% hydrochloric acid (2 ml), and extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), and concentrated. The residue was recrystallised from methanol to give (12b) (45 mg, 56%), m.p. 138—140 °C, which was identical with a sample obtained from (3c).

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