Preparation and Structure of Some *cis*-fused Ureas: *cis*-Perhydrothieno-[3,4-*d*]imidazol-2-one *SS*-Dioxides

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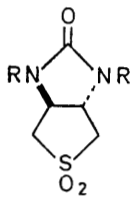
A general route to the title compounds has been developed. This involves cyclisation of 2,3-dihydro-3-ureidothiophen *SS*-dioxides (20) with base. Both symmetrically and unsymmetrically substituted *cis*-fused ureas (2) can be prepared. A similar base-induced reaction of the corresponding 3-carbamoyl-2,3-dihydrothiophen *SS*-dioxides led, *via* the corresponding cyclic carbamates (8), by a route involving elimination and double-bond migration, to the corresponding 4-amino-2,3-dihydrothiophen *SS*-dioxides (11).

THE preparation of the *trans*-fused ureas (1) has recently been described.[1] The synthesis of the corresponding *cis*-fused ureas (2) was also desirable as a possible route



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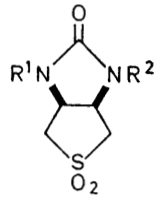

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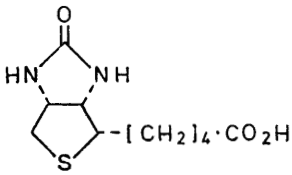

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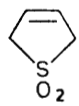

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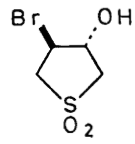

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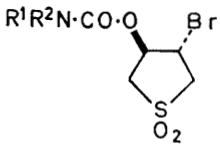

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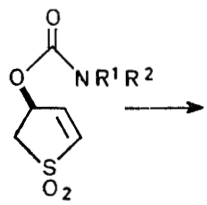

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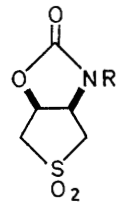

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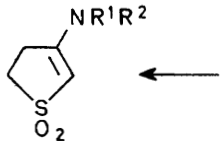

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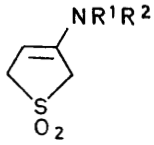

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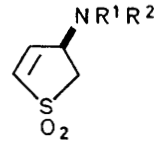
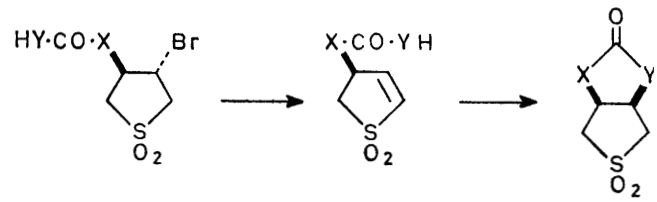


(9)

to biotin (3) and its analogues.[2] Since addition reactions to 2,3-dihydrothiophen *SS*-dioxides are well established,[3] intramolecular additions to appropriately substituted 2,3-dihydrothiophen *SS*-dioxides (Scheme) have been investigated.

2,5-Dihydrothiophen dioxide (4) was converted with bromine water into the known bromohydrin (5);[4] on heating this with phenyl isocyanate the corresponding phenylcarbamate (6; $R^1 = H$, $R^2 = Ph$) was formed.



SCHEME

On treating the carbamate with sodium ethoxide in ethanol a new product was formed which was assigned the enamine structure (11; $R^1 = H$, $R^2 = Ph$) on the basis of its ^1H n.m.r. and other spectral properties. The mechanism proposed for this conversion involves an initial dehydrobromination to give the unsaturated sulphone (7; $R^1 = H$, $R^2 = Ph$), followed by formation of the cyclic carbamate (8; R = Ph). Further reaction with base abstracts a proton α to the sulphone group with subsequent elimination, by ring opening, of the carbamate group, followed by loss of carbon dioxide. The conjugated olefin (9; $R^1 = H$, $R^2 = Ph$) initially formed can equilibrate by αβ ⟶ βγ double-bond isomerisation,[5] leading to migration of the olefinic bond *via* the unstable enamine (10; $R^1 = H$, $R^2 = Ph$) into the most stable position, *viz.* to form the vinylogous sulphonamide (11; $R^1 = H$, $R^2 = Ph$). That such a series of reactions was occurring was established by varying the way in which the starting carbamate (6; $R^1 = H$, $R^2 = Ph$) was treated with base. Slow addition of 1 equiv. of triethylamine to the carbamate eliminated hydrogen bromide to form the allylic phenylcarbamate (7; $R^1 = H$, $R^2 = Ph$), identified by comparison with authentic material prepared from the allylic alcohol (12)[6] and phenyl isocyanate. The allylic carbamate readily cyclised to the cyclic carbamate (8; R = Ph) on prolonged treatment with triethylamine; heating the latter with an excess of tri-

[1] F. Ellis, P. G. Sammes, M. B. Hursthouse, and S. Neidle, *J.C.S. Perkin I*, 1972, 1560.

[2] For example, S. A. Harris, D. E. Wolf, R. Mozingo, G. E. Arth, R. C. Anderson, N. R. Easton, and K. Folkers, *J. Amer. Chem. Soc.*, 1945, **67**, 2096; M. W. Goldberg and L. H. Sternbach, U.S.P. 2,489,235/1949 (*Chem. Abs.*, 1951, **45**, 185).

[3] H. E. Faith, M. P. Kautsky, and B. E. Abreu, *J. Org. Chem.*, 1962, **27**, 2889; C. S. Argyle, S. C. Goodby, K. G. Mason, R. A. Reed, M. A. Smith, and E. S. Stern, *J. Chem. Soc.* (*C*), 1967, 2156.

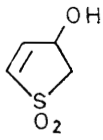
[4] O. E. van Lohuisen and H. J. Backer, *Rec. Trav. chim.*, 1949, **68**, 1137.

[5] D. E. O'Connor and W. I. Lyness, *J. Amer. Chem. Soc.*, 1964, **86**, 384.

[6] M. Prochazka and V. Horak, *Coll. Czech. Chem. Comm.*, 1959, **24**, 1509.

ethylamine in ethanol catalysed the conversion of (8; R = Ph) into the allylic amine (9; $R^1 = H$, $R^2 =$ Ph). All the intermediates in this sequence were converted by sodium ethoxide in ethanol into the vinylogous sulphonamide (11; $R^1 = H$, $R^2 =$ Ph). Although migration of the double bond in intermediates of the type (9) to give the isomer (11) must proceed *via* the βγ-unsaturated isomer (10), no evidence that the latter could exist as a stable intermediate was found. Acetylation of the vinylogous sulphonamide (11; $R^1 = H$, $R^2 =$ Ph) with acetyl chloride afforded the *N*-acetyl derivative (11; $R^1 =$ Ac, $R^2 =$ Ph). Basic hydrolysis of this anilide liberated the starting enamine; acidic hydrolysis, with 2N-hydrochloric acid, converted it into the ketone (13) [7] and acetanilide.

Ethyl chloroformate reacted with the bromohydrin (5), in the presence of 1 equiv. of triethylamine, to give the ethyl carbonate (14), but use of an excess of the base afforded the allylic ester (15) by elimination of hydrogen bromide. Neither of these carbonates reacted with ammonia, aniline, or methylamine to give a carbamate. Use of more vigorous conditions caused eliminations. A general preparation of the carbamates was achieved,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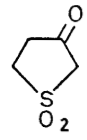
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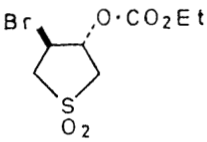
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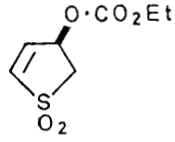
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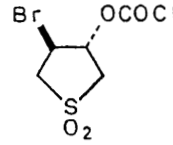
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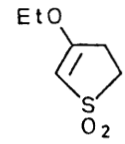
however, by use of the chloroformate (16), prepared by the reaction of the bromohydrin (5) with phosgene in the presence of quinoline. The chloroformate (16) reacted with aniline to give the same carbamate (6; $R^1 = H$, $R^2 =$ Ph) as before. Benzylamine, methylamine, and dimethylamine reacted similarly to give the corresponding carbamates; treatment with ammonia gave the unsaturated carbamate (7; $R^1 = R^2 = H$) directly. On treatment of the secondary carbamates from benzylamine and methylamine with sodium ethoxide in ethanol the corresponding enamines (11; $R^1 = H$, $R^2 = PhCH_2$) and (11; $R^1 = H$, $R^2 =$ Me) were produced in high yields. Similar treatment of the primary carbamate (7; $R^1 = R^2 = H$) did not produce the corresponding enamine (11; $R^1 = R^2 = H$), but this was not surprising, since the amine (9; $R^1 = R^2 = H$) is known to undergo dimerisation.[8] An intramolecular addition reaction is not possible with the tertiary carbamate (6; $R^1 = R^2 =$ Me); treatment of this with ethoxide afforded the vinylic ether (17).

[7] K. G. Mason, M. A. Smith, E. S. Stern, and J. A. Elvidge, *J. Chem. Soc.* (*C*), 1967, 2171.

This reaction probably proceeds by an elimination–addition mechanism. Treatment of the dimethylcarbamate (6; $R^1 = R^2 =$ Me) with aqueous sodium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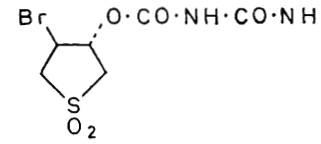
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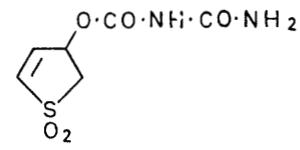
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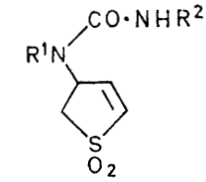
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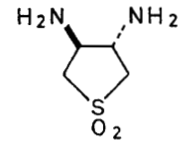
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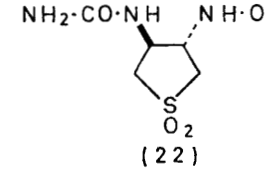
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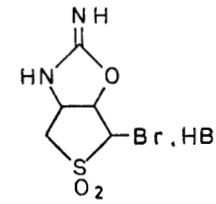
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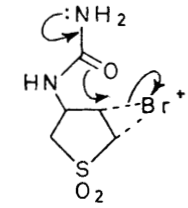
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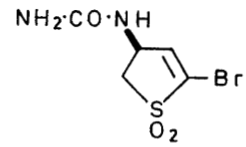
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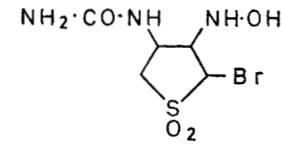
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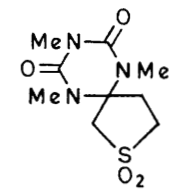
(27)

carbonate produced the allylic amine (9; $R^1 = R^2 =$ Me), identical with the compound prepared by Bailey and Cummins from the reaction of thiophen dioxide with dimethylamine.[9] This amine (9; $R^1 = R^2 =$ Me) was

[8] M. Prochazka and V. Horak, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2278.

[9] W. J. Bailey and E. W. Cummins, *J. Amer. Chem. Soc.*, 1954, **76**, 1932.

isomerised to the enamine (11; $R^1 = R^2 = Me$) with sodium ethoxide in ethanol.

The chloroformate (16) reacted with urea to give the allophanate (18), which could also be dehydrobrominated under mild basic conditions (aqueous quinoline) to produce the allylic allophanate (19). Warming the latter compound with aqueous sodium hydrogen carbonate produced the allylic urea (20; $R^1 = R^2 = H$); in this case reaction probably proceeds *via* the cyclic carbamate (8; $R = NH_2{\cdot}CO$), which was not isolated.

On treatment with a stronger base, such as sodium carbonate, cyclisation of the allylic urea (20; $R^1 = R^2 = H$) into the isomer (2; $R^1 = R^2 = H$) occurred. In view of its mode of formation this compound must have the *cis*-fused structure. Comparison with the known *trans*-compound (1; $R = H$),[1] prepared from the *trans*-3,4-dibromotetrahydrothiophen dioxide with ammonia and phosgene, showed them to be isomeric. The former, *cis*-fused isomer showed $\nu_{max.}$ 1710 cm^{-1} for its carbonyl absorption, whereas the latter showed $\nu_{max.}$ 1705 and 1690 cm^{-1}. The ^1H n.m.r. spectrum of the *trans*-fused isomer showed a complex pattern for the ring protons, with multiplets centred at τ 5·05 (2H) and 6·05 (4H). In contrast, the *cis*-fused urea showed two very broad peaks centred at τ 5·5 (2H) and 6·9 (4H). The lack of fine structure in the case of the *cis*-isomer is attributed to a conformational 'flipping' of the sulphone groups between two extremes [(2a) ⇌ (2b)] as illustrated by Dreiding models. In contrast,

(2a) (2b)

the *trans*-fused isomer (1; $R = H$) is rigid. The low solubility of the *cis*-fused urea (2; $R^1 = R^2 = H$) in most solvents precluded low temperature n.m.r. studies.

The chemical difference between the *cis*- and the strained *trans*-fused ureas was demonstrated by the action of boiling 6N-hydrochloric acid. The *trans*-urea was quantitatively hydrolysed in 24 h to the *trans*-diamine (21), isolated as the hydrochloride salt. Under the same conditions the *cis*-compound merely formed the urea hydrochloride, from which the starting material could be regenerated by treatment with weak base. The stability of the *cis*-fused urea to attempted hydrolysis is reminiscent of that recorded for biotin, which requires treatment with barium hydroxide at 140°.[10]

The *cis*-fused urea (2; $R^1 = R^2 = H$) readily reacted with acetyl chloride to give both mono- (2; $R^1 = H$, $R^2 = Ac$) and di-acetyl (2; $R^1 = R^2 = Ac$) derivatives.

The allylic urea (20; $R^1 = R^2 = H$) is also an intrinsically useful compound since strong nucleophiles can add to the unsaturated sulphone system, as demonstrated by addition of hydroxylamine to give the adduct (22). Bromine also reacted with the allylic urea (20; $R^1 = R^2 = H$), but the product was that of electrophilic addition, the bromothieno-oxazole hydrobromide (23), probably formed *via* the intermediate (24). Interestingly, with 1 equiv. of base compound (23) spontaneously underwent ring opening to give the allylic urea (25), reflecting the acidity of the proton at position 6 in the salt (23). The bromo-derivative (25) reacted with hydroxylamine to give the adduct (26). A similar base-catalysed reversal of the cyclisation step in the thienoimidazole series, *viz.* (2; $R^1 = R^2 = H$) ⟶ (20; $R^1 = R^2 = H$), was not observed.

In order to prepare other *cis*-fused cyclic ureas, the allylic amines (9; $R^1 = H$, $R^2 = Ph$) and (9; $R^1 = H$, $R^2 = Me$) were treated with either phenyl isocyanate or methyl isocyanate. In this way the ureas (20; $R^1 = R^2 = Me$), (20; $R^1 = R^2 = Ph$), and (20; $R^1 = Ph$, $R^2 = Me$) were prepared and, by further treatment with base, cyclised to the corresponding *cis*-fused ureas.

An interesting reaction occurred between the vinylic amine (11; $R^1 = H$, $R^2 = Me$) and methyl isocyanate. Two equiv. of the isocyanate reacted in the presence of sodium hydride to give the spiro-derivative (27), a reaction which again demonstrates the susceptibility of the double bond of 2,3-dihydrothiophen dioxides to addition reactions.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were determined for Nujol mulls unless otherwise stated. ^1H N.m.r. spectra were recorded with a Varian T60 instrument for solutions in deuteriochloroform containing tetramethylsilane as internal reference unless otherwise stated. Light petroleum refers to the fraction of boiling range 60—80°.

3-Bromotetrahydro-4-hydroxythiophen 1,1-Dioxide (5).—Bromine (38 g) in water (5 l) and 2,5-dihydrothiophen dioxide (24 g) were kept together at 5° for 3 days. The crystalline precipitate (34 g, 77%) crystallised from methanol to give the bromohydrin, m.p. 189—190° (lit.,[4] 189—190°), $\nu_{max.}$ 3450, 1295, and 1120 cm^{-1}.

4-Bromotetrahydro-3-thienyl Phenylcarbamate SS-Dioxide (6; $R^1 = H$, $R^2 = Ph$).—3-Bromotetrahydro-4-hydroxythiophen 1,1-dioxide (4 g) was heated with phenyl isocyanate (3·3 g.) until all the solid dissolved. The mixture was cooled to give a white solid which was triturated with hot light petroleum to remove the excess of phenyl isocyanate. The residue crystallised from toluene (*ca.* 200 ml) to give the *carbamate* (5·7 g, 92%), m.p. 153—154°, $\nu_{max.}$ 3330, 1600, 1530, 1310, and 1125 cm^{-1}, τ 2·7 (5H, m), 2·95br (1H, exchanged with D_2O), 4·4 (1H, m), 5·3 (1H, m), and 5·9—6·9 (4H, m) (Found: C, 39·6; H, 3·65; N, 4·2. $C_{11}H_{12}BrNO_4S$ requires C, 39·5; H, 3·6; N, 4·2%).

4-Anilino-2,3-dihydrothiophen 1,1-Dioxide (11; $R^1 = H$, $R^2 = Ph$).—The carbamate (6; $R^1 = H$, $R^2 = Ph$) (2·3 g) was stirred overnight with ethanol (80 ml) in which sodium (0·65 g) had been dissolved. The white suspension was evaporated to dryness, water was added to the residue, and the product was extracted with chloroform. After evaporation of the extract, the *amine* (1·4 g, 97%) was crystallised from ethanol; m.p. 162—163°, $\nu_{max.}$ 3300,

[10] K. Hofmann, D. B. Melville, and V. du Vigneaud, *J. Biol. Chem.*, 1941, **141**, 207.

1620, 1595, 1500, 1290, and 1100 cm^{-1}, τ 2·7 (5H, m), 3·2br (1H, exchanged with D_2O), 4·2 (1H, s), and 6·5—7·2 (4H, m) (Found: C, 57·4; H, 5·4; N, 6·5; S, 15·3. $C_{10}H_{11}NO_2S$ requires C, 57·4; H, 5·3; N, 6·7; S, 15·3%).

2,3-Dihydro-3-thienyl Phenylcarbamate SS-Dioxide (7; R^1 = H, R^2 = Ph).—2,3-Dihydro-3-hydroxythiophen 1,1-dioxide [6] (1 g) was heated with phenyl isocyanate (1·5 g) 5 min under reflux. The mixture was cooled and triturated with light petroleum to remove phenyl isocyanate. The residue was purified by precipitation from benzene with light petroleum to give the *allylic carbamate* (1·38 g, 75%), m.p. 114—115°, $\nu_{max.}$ 3370, 1725, 1655, 1600, 1500, 1300, and 1150 cm^{-1}, τ 2·6 (5H, s), 2·7br (1H, s), 3·15 (2H, s and d, *J* 2 Hz), 3·95 (1H, m), 6·0—6·9 (2H, dq, J_{AB} 14, J_{AX} 7, J_{BX} 4 Hz) (Found: C, 52·4; H, 4·5; N, 5·4. $C_{11}H_{11}NO_4S$ requires C, 52·2; H, 4·4; N, 5·5%). The allylic carbamate (146 mg) was treated with sodium ethoxide in ethanol to yield 4-anilino-2,3-dihydrothiophen 1,1-dioxide (108 mg, 90%), m.p. 162—163°.

Hexahydro-3-phenylthieno[3,4-d]oxazol-2-one 5,5-Dioxide (8; R = Ph).—To a solution of the carbamate (6; R^1 = H, R^2 = Ph) (1·5 g) in chloroform (20 ml) was added triethylamine (0·94 g). After 2 h the mixture was filtered and the residue washed with chloroform to remove amine hydrobromide. The product was crystallised from acetonitrile to give the *cyclic carbamate* (1·07 g, 94%), m.p. 191—193°, $\nu_{max.}$ 1740, 1600, 1500, 1325, and 1135 cm^{-1}, τ [$(CD_3)_2SO$] 2·3—3·0 (5H, m), 4·4—4·8 (2H, m), and 6·2—7·0 (4H, m) (Found: C, 52·1; H, 4·3; N, 5·5. $C_{11}H_{11}NO_4S$ requires C, 62·2; H, 4·4; N, 5·5%). The cyclic carbamate (169 mg) was treated with sodium ethoxide in ethanol (20 ml) to yield 4-anilino-2,3-dihydrothiophen 1,1-dioxide (11; R^1 = H, R^2 = Ph) (140 mg, 99%). One equiv. of triethylamine in chloroform was added dropwise during 2 h to a solution of the carbamate (6; R^1 = H, R^2 = Ph) (1 equiv.) in chloroform. T.l.c. of the solution (SiO_2; 5% MeOH–$CHCl_3$) showed it to contain a mixture of 2,3-dihydro-3-thienyl phenylcarbamate *SS*-dioxide (7; R^1 = H, R^2 = Ph) and hexahydro-3-phenylthieno[3,4-*d*]-oxazol-2-one 5,5-dioxide.

3-Anilino-2,3-dihydrothiophen 1,1-Dioxide (9; R^1 = H, R^2 = Ph).—The carbamate (6; R^1 = H, R^2 = Ph) (568 mg) and triethylamine (361 mg) were heated together under reflux in ethanol (20 ml) for 3 h. The solvent and excess of amine were evaporated off, water was added to the residue, and the product was extracted with chloroform. The dried organic phase was evaporated to dryness and the solid (294 mg, 85%) crystallised from benzene to give the *allylic amine*, m.p. 133—134°, $\nu_{max.}$ 3375, 3100, 1605, 1505, 1290, and 1120 cm^{-1}, τ 2·7 (2H, m), 3·2 (5H, m), 5·0 (1H, m), 6·0—7·0 (2H, dq, J_{AB} 14, J_{AX} 7, J_{BX} 4 Hz), and 6·1br (1H, exchanged with D_2O) (Found: C, 57·6; H, 5·2; N, 6·6; S, 15·3. $C_{10}H_{11}NO_2S$ requires C, 57·4; H, 5·3; N, 6·7; S, 15·3%). Under similar conditions the thienooxazolone (8; R = Ph) gave the same product. On treatment with sodium ethoxide in ethanol the cyclic carbamate was quantitatively isomerised to 4-anilino-2,3-dihydrothiophen 1,1-dioxide.

4-N-Acetylanilino-2,3-dihydrothiophen 1,1-Dioxide (11; R^1 = Ac, R^2 = Ph).—4-Anilino-2,3-dihydrothiophen 1,1-dioxide (703 mg) was heated under reflux with acetyl chloride (4 ml) for 2 h. The acetyl chloride was evaporated off and the residue crystallised from a large volume of ethanol to give the *N-acetyl derivative* (705 mg, 84%), m.p. 171—173°, $\nu_{max.}$ 3110w, 1700, 1600, 1490, 1280, and 1095 cm^{-1}, τ 2·2—2·8 (5H, m), 3·3 (1H, s), 6·5—7·2 (4H, m), and 8·1 (3H, s) (Found: C, 57·1; H, 5·25; N, 5·5. $C_{12}H_{13}NO_3S$ requires C, 57·35; H, 5·2; N, 5·6%). The *N*-acetyl derivative (96 mg) was stirred overnight at room temperature with N-sodium hydroxide (1 ml) and ethanol (2 ml). The solvents were evaporated off and water was added to the residue. The aqueous phase was extracted with chloroform; evaporation of the extract gave 4-anilino-2,3-dihydrothiophen 1,1-dioxide.

Treatment of the *N*-acetyl derivative (104 mg) at room temperature with 2N-hydrochloric acid (4 ml) and ethanol (4 ml) for 16 h afforded a sticky product, which t.l.c. (SiO_2; 5% MeOH–$CHCl_3$) showed to be a mixture of an unknown compound and acetanilide, the latter being isolated by crystallisation from light petroleum. Upon addition of Brady's reagent to the residual mother liquor, a yellow derivative formed which was crystallised from acetic acid; m.p. 208—209° (lit. m.p.s of dinitrophenylhydrazone of tetrahydrothiophen-3-one 1,1-dioxide are 211—213 [11] and 205—207° [7]). The reaction mixture showed $\nu_{max.}$ 3300, 1660, 1600, 1560, 1500 (assigned to acetanilide), 1760, 1335, and 1130 cm^{-1}, τ 1·8br (1H, s), 2·3—3·1 (5H, m), 7·9 (3H, s) (acetanilide), 6·3 (2H, s), 6·4 (2H, m), and 6·9 (2H, m).

4-Bromotetrahydro-3-thienyl Ethyl Carbonate SS-Dioxide (14).—To a suspension of 3-bromotetrahydro-4-hydroxythiophen 1,1-dioxide (350 mg) in chloroform (6 ml) containing ethyl chloroformate (180 mg) cooled below 10°, a solution of triethylamine (166 mg) in chloroform (6 ml) was added during 1 h. The resulting solution was evaporated to dryness and the residue extracted with ethyl acetate. Evaporation yielded the product contaminated with bromohydrin, which was removed by dissolving the product in dichloromethane, filtering, and evaporating to dryness. The product crystallised from ethanol to give the *ethyl carbonate*, m.p. 108—109°, $\nu_{max.}$ 1740, 1310, and 1150 cm^{-1}, τ 4·5 (1H, m), 5·7 (2H, q, *J* 6 Hz), 5·1—6·9 (5H, m), and 8·6 (3H, t, *J* 6 Hz) (Found: C, 29·1; H, 4·05. $C_7H_{11}BrO_5S$ requires C, 29·3; H, 3·9%).

2,3-Dihydro-3-thienyl Ethyl Carbonate SS-Dioxide (15).—To an ice-cold suspension of 3-bromotetrahydro-4-hydroxythiophen 1,1-dioxide (2·24 g) in chloroform (100 ml) were added triethylamine (2·1 g) and ethyl chloroformate (1·13 g). After stirring for 2 h the solvent was evaporated off and the residue extracted with ethyl acetate. The extracts were evaporated to dryness to give an oil, which was distilled under reduced pressure to give the *allylic carbonate*, b.p. 164° at 2 mmHg, n_D^{24} 1·4843, $\nu_{max.}$ (film) 3080, 2980, 1750, 1615, 1310, 1260, 1150, and 1100 cm^{-1}, τ 3·2 (2H, s and d, *J* 2 Hz), 4·35 (1H, m), 5·75 (2H, q, *J* 7 Hz), 6·0 and 6·95 (2H, dq, J_{AB} 14, J_{AX} 7, J_{BX} 4 Hz), and 8·65 (3H, t, *J* 7 Hz) (Found: C, 40·7; H, 5·0. $C_7H_{16}O_5S$ requires C, 40·8; H, 4·9%).

4-Bromotetrahydro-3-thienyl Chloroformate SS-Dioxide (16).—Finely powdered 3-bromotetrahydro-4-hydroxythiophen 1,1-dioxide (20 g) and a solution of quinoline (14 g) in dry benzene (50 ml) were simultaneously added during 2 h to a stirred, ice-cooled solution of phosgene (*ca.* 100 g) in dry benzene (500 ml). The suspension was then stirred at room temperature for 3 h. The mixture was washed with 5N-hydrochloric acid (2 × 50 ml) and water (100 ml), filtered to remove unchanged bromohydrin (2·05 g), and dried (Na_2SO_4). The benzene solution was evaporated to dryness to give a pale yellow solid (20·22 g; 87% based

[11] M. Prochazka, *Coll. Czech. Chem. Comm.*, 1960, **25**, 465.

on reacted material). The chloroformate was not further purified for reactions. A small sample was sublimed under reduced pressure (120° at 0·5 mmHg) to give *material* of m.p. 93—95°, $\nu_{max.}$ 1760, 1320, 1165, and 1130 cm^{-1}, τ 4·3 (1H, m), 5·3 (1H, m), and 5·8—6·8 (4H, m) (Found: C, 21·7; H, 2·1. $C_5H_6BrClO_4S$ requires C, 21·6; H, 2·2%).

4-Bromotetrahydro-3-thienyl Phenylcarbamate SS-*Dioxide* (6; R^1 = H, R^2 = Ph).—To a solution of the chloroformate (16) (560 mg.) in benzene (21 ml) was added a solution of distilled aniline (375 mg) in benzene (9 ml). The mixture was stirred for 1 h, then filtered, and the residue was washed well with hot ethyl acetate. The combined filtrates were evaporated to dryness to give a white solid (649 mg; 96%) which was crystallised from toluene to give the phenylcarbamate, identical with that prepared from phenyl isocyanate.

4-Bromotetrahydro-3-thienyl Benzylcarbamate SS-*Dioxide* (6; R^1 = H, R^2 = PhCH$_2$).—To a solution of the chloroformate (16) (2·77 g) in benzene (70 ml) was added a solution of benzylamine (2·14 g) in benzene (30 ml). A white precipitate formed and stirring was continued for 1 h. The mixture was filtered and the residue washed with benzene. The filtrate was evaporated to dryness and the *benzylcarbamate* (3·33 g, 96%) crystallised from benzene; m.p. 120—121°, $\nu_{max.}$ 3350, 1700, 1550, 1340, and 1150 cm^{-1}, τ 2·6 (5H, s), 4·0—4·6br (1H), 4·5 (1H, m), 5·4br (1H, exchanged slowly with D_2O), 5·6 (2H, d), and 6·0—7·0 (4H, m) (Found: C, 41·4; H, 4·0; N, 4·0. $C_{12}H_{14}BrNO_4S$ requires C, 41·4; H, 4·05; N, 4·0%).

4-Bromotetrahydro-3-thienyl Methylcarbamate SS-*Dioxide* (6; R^1 = H, R^2 = Me).—A solution of methylamine (0·31 g) in benzene (20 ml) was slowly added during 20 min to an ice-cold solution of the chloroformate (16) (1·36 g) in benzene (50 ml). The mixture was stirred for 1 h then filtered, and the residue was extracted with hot benzene. Evaporation of the extracts gave the *methylcarbamate* (1·18 g, 88%), which was crystallised from ethanol; m.p. 96—97°, $\nu_{max.}$ 3370, 1700, 1320, and 1140 cm^{-1}, τ 4·3 (1H, m), 4·8br (1H, exchanged with D_2O), 5·2 (1H, m), 5·8—6·8 (4H, m), and 7·0 (3H, d) (Found: C, 26·8; H, 3·7; N, 5·1. $C_6H_{10}BrNO_4S$ requires C, 26·5; H, 3·7; N, 5·2%).

2,3-*Dihydro-3-thienyl Carbamate* SS-*Dioxide* (7; R^1 = R^2 = H).—Ammonia gas was passed through a solution of the chloroformate (16) (2·77 g) in benzene (100 ml) for 5 min at room temperature. A white precipitate was formed and stirring was continued for 2 h. The precipitate was filtered off and extracted with ethyl acetate; the extract was evaporated to give the *carbamate* (1·72 g, 97%), m.p. 148—150° (from acetonitrile), $\nu_{max.}$ 3460, 3370, 3210w, 1710, 1615, 1300, and 1150 cm^{-1}, τ [(CD$_3$)$_2$SO] 2·6—3·4 (2H, m), 3·2br (2H, exchanged with D_2O), 4·1 (1H, m), and 6·0—7·0 (2H, dq, J_{AB} 14, J_{AX} 7, J_{BX} 4 Hz) (Found: C, 34·1; H, 4·0; N, 7·8. $C_5H_7NO_4S$ requires C, 33·9; H, 4·0; N, 7·9%).

4-Bromotetrahydro-3-thienyl Dimethylcarbamate SS-*Dioxide* (6; R^1 = R^2 = Me).—To an ice-cooled solution of the chloroformate (16) (4·5 g) in dry benzene (50 ml) was added a cooled solution of dimethylamine (1·57 g) in benzene (20 ml) during 1 h. The mixture was stirred at room temperature for 16 h and filtered. The residue was washed with dry benzene and the filtrate evaporated to dryness to give the *dimethylcarbamate* (3·68 g, 80%), m.p. 128—129° (from benzene), $\nu_{max.}$ 1705, 1320, and 1130 cm^{-1}, τ 4·5 (1H, m), 5·3 (1H, m), 5·9—6·9 (4H, m), and 7·1 (6H, s) (Found: C, 29·5; H, 4·2; Br, 27·9; N, 4·8; S, 11·4. $C_7H_{12}BrNO_4S$ requires C, 29·4; H, 4·2; Br, 27·9; N, 4·9; S, 11·2%).

4-Benzylamino-2,3-dihydrothiophen 1,1-*Dioxide* (11; R^1 = H, R^2 = PhCH$_2$).—The benzylcarbamate (6; R^1 = H, R^2 = PhCH$_2$) (696 mg) was stirred overnight at room temperature with ethanol (26 ml) containing sodium (184 mg). The mixture was evaporated to dryness, water was added to the residue, and the product was extracted with chloroform. The extracts were evaporated to dryness to give the *vinylogous benzylsulphonamide* (445 mg, 97%), m.p. 164—166° (from methanol), $\nu_{max.}$ 3350, 1615, 1550, 1365, and 1105 cm^{-1}, τ 2·7 (5H, m), 4·7 (1H, m), and 6·6—7·3 (4H, m) (Found: C, 59·2; H, 5·8; N, 6·2. $C_{11}H_{13}NO_2S$ requires C, 59·2; H, 5·9; N, 6·3%).

2,3-*Dihydro-4-methylaminothiophen* 1,1-*Dioxide* (11; R^1 = H, R^2 = Me).—The methylcarbamate (6; R^1 = H, R^2 = Me) (0·54 g) treated as in the preceding experiment, afforded the *vinylogous methylsulphonamide* (252 mg, 85%), m.p. 157—159° (from ethanol), $\nu_{max.}$ 3380, 1615, 1240, and 1100 cm^{-1}, τ (D_2O) 4·9 (1H, s), 6·5—6·9 (2H, m), 6·9—7·3 (2H, m), and 7·4 (3H, s) (Found: C, 40·7; H, 6·0; N, 9·5. $C_5H_9NO_2S$ requires C, 40·8; H, 6·2; N, 9·5%).

4-Ethoxy-2,3-dihydrothiophen 1,1-*Dioxide* (17).—The dimethylcarbamate (6; R^1 = R^2 = Me) (426 mg) was stirred overnight with ethanol (25 ml) containing sodium (120 mg). The mixture was evaporated to dryness, water was added, and the product was extracted with chloroform. The extracts were evaporated to dryness to give an oil which solidified. The *ethyl ether* had m.p. 65—66° (from carbon tetrachloride), $\nu_{max.}$ 3100, 1615, 1350, and 1110 cm^{-1}, τ 4·3 (1H, s), 6·0 (2H, q, J 7 Hz), 6·6 (2H, m), 7·1 (2H, m), and 8·6 (3H, t, J 7 Hz) (Found: C, 44·25; H, 6·2; S, 19·9. $C_6H_{10}O_3S$ requires C, 44·4; H, 6·2; S, 19·8%).

3-*Dimethylamine-2,3-dihydrothiophen* 1,1-*Dioxide* (9; R^1 = R^2 = Me).—The dimethylcarbamate (6; R^1 = R^2 = Me) (98 mg) was warmed at 60° with 10% sodium carbonate solution (5 ml) until a clear solution had formed. The solution was cooled and extracted with chloroform to yield an oil which slowly crystallised. The product, m.p. 64—65°, was identical with the amine prepared by the method of Bailey and Cummins.[9]

4-Dimethylamino-2,3-dihydrothiophen 1,1-*Dioxide* (11; R^1 = R^2 = Me).— 3-Dimethylamino-2,3-dihydrothiophen 1,1-dioxide (303 mg) was stirred overnight at room temperature with ethanol (20 ml) containing sodium (87 mg). The solvent was evaporated off, water was added, and the product was extracted with chloroform. The extracts were evaporated to dryness to give the *amine* (289 mg), m.p. 171—172° (from ethanol), $\nu_{max.}$ 3100w, 1600, 1280, and 1105 cm^{-1}, τ 4·8 (1H, s), 6·4—7·2 (4H, m), and 7·1 (6H, s) (Found: C, 44·5; H, 6·7; N, 8·7. $C_6H_{11}NO_2S$ requires C, 44·7; H, 6·8; N, 8·7%).

4-Bromotetrahydro-3-thienyl Allophanate SS-*Dioxide* (18).—An intimately ground mixture of 4-bromotetrahydro-3-thienyl chloroformate SS-dioxide (2·77 g) and urea (1·2 g) was heated at *ca.* 100° for 24 h. The mixture fused, bubbled, and finally solidified. The cooled residue was washed with hot acetone, cold water, and acetone again to give the white *allophanate* (1·96 g, 65%), m.p. 201—202° (from water), $\nu_{max.}$ 3450, 3350, 1740, 1690, 1605, 1320, and 1130 cm^{-1}, τ (CF_3·CO_2H) 1·4br (1H), 2—4 (broad hump, 2H), 4·8 (1H, m), 5·7 (1H, m), and 6·1—7·1 (4H, m) (Found: C, 24·3; H, 3·1; N, 9·4. $C_6H_9N_2BrO_5S$ requires C, 23·9; H, 3·0; N, 9·3%).

2,3-*Dihydro-3-thienyl Allophanate* SS-*Dioxide* (19).—

4-Bromotetrahydro-3-thienyl allophanate *SS*-dioxide (934 mg) was heated under reflux with quinoline (640 mg) and water (10 ml) for 2 h. The mixture was cooled, N-sodium hydroxide solution (3·1 ml) was added, and the water was removed under reduced pressure. The residue was washed with ether to remove quinoline and the *allophanate* (497 mg, 73%) crystallised from water; m.p. 170—172°, $\nu_{max.}$ 3400, 3310, 3240, 1760, 1710, 1600, 1320, and 1170 cm^{-1}, τ (CF_3·CO_2H) 3·5 (2H, m), 4·8 (1H, m), 4·8br (1H, exchanged with D_2O), 6·7br (2H, exchanged with D_2O), and 6·7 (2H, dq, J_{AB} 14, J_{AX} 7, J_{BX} 4 Hz) (Found: C, 32·7; H, 3·7; N, 12·6; S, 14·5. $C_6H_8N_2O_5S$ requires C, 32·7; H, 3·7; N, 12·7; S, 14·55%).

2,3-*Dihydro*-3-*thienylurea* SS-*Dioxide* (20; $R^1 = R^2 =$ H).—4-Bromotetrahydro-3-thienyl allophanate *SS*-dioxide (2 g) was stirred in water (30 ml) at 65°. Solid sodium hydrogen carbonate (560 mg) was added during 0·5 h and stirring was continued for a further 4·5 h to give a clear solution. The solvent was removed under reduced pressure and the residue crystallised from water to give the *allylic urea* (913 mg, 78%), m.p. 195—197°, $\nu_{max.}$ 3480, 3380, 3300, 3080, 1660, 1560, 1295, and 1120 cm^{-1}, τ (CF_3·CO_2H) 3·5 (2H, s and d J 1 Hz), 5·0 (1H, m), and 6·2—7·2 (2H, dq, J_{AB} 14, J_{AX} 7, J_{BX} 4 Hz) (Found: C, 34·1; H, 4·6; N, 15·8; S, 18·35. $C_5H_8N_2O_3S$ requires C, 34·1; H, 4·6; N, 15·9; S, 18·2%).

Under similar conditions 2,3-dihydro-3-thienyl allophanate *SS*-dioxide (19) was also converted into the allylic urea.

cis-*Hexahydro*[3,4-d]*imidazol*-2-*one* 5,5-*Dioxide* (2; $R^1 = R^2 =$ H).—4-Bromotetrahydro-3-thienyl allophanate *SS*-dioxide (3 g) and anhydrous sodium carbonate (1·27 g) were heated under reflux for 2 h in water (20 ml). The solution was cooled and evaporated to dryness, and the residue crystallised from water to give the *cyclic urea* (0·8 g, 45%), m.p. 318—320° (sealed and evacuated tube), $\nu_{max.}$ 3200, 3100, 1710, 1325, and 1150 cm^{-1}, τ (CF_3·CO_2H) 5·5br (2H) and 6·9br (4H), *m/e* 176 (Found: C, 34·05; H, 4·8; N, 16·0; S, 18·35. $C_5H_8N_2O_3S$ requires C, 34·1; H, 4·6; N, 15·9; S, 18·2%).

Under similar conditions both the allylic allophanate (19) and the allylic urea (20; $R^1 = R^2 =$ H) were converted into the same cyclic urea.

Acidic Hydrolysis of cis- *and* trans-*Hexahydrothieno*-[3,4-d]*imidazol*-2-*one* 5,5-*Dioxides*.—The cyclic urea (176 mg) was heated under reflux overnight with 6N-hydrochloric acid (6 ml). The acid was removed under reduced pressure to give a white solid. The product from the *cis*-urea (213 mg), crystallised from water, had $\nu_{max.}$ 3500—2300, 1700, 1320, and 1140 cm.$^{-1}$. The analysis showed that the crystallised material was probably a mixture of the free urea and the hydrochloride, though the C : N ratio was exactly 5 : 2, showing that the carbonyl group had not been lost. When the product was suspended in dilute aqueous base the starting material was regenerated. The product from the *trans*-urea [1] (234 mg), crystallised from 2 : 3 water–ethanol, had m.p. 302—304°, $\nu_{max.}$ 3500—2400, 1310, and 1180 cm^{-1} (Found: C, 21·6; H, 5·4; Cl, 31·6; N, 12·5. Calc. for $C_4H_{12}Cl_2N_2O_2S$: C, 21·5; H, 5·4; Cl, 31·8; N, 12·6%).

1,3-*Diacetylhexahydrothieno*[3,4-d]*imidazol*-2-*one* SS-*Dioxide* (2; $R^1 = R^2 =$ Ac).—Hexahydrothieno[3,4-*d*]imidazol-2-one 5,5-dioxide (314 mg) was boiled under reflux with acetyl chloride (5 ml) in acetic acid (7·5 ml) for 4 h. The solvents were removed under reduced pressure and the residue was washed free of acid with ether. The *diacetyl derivative* (300 mg, 67%) had m.p. 236—238° (from methanol), $\nu_{max.}$ 1745, 1695, 1330, 1310, and 1150 cm^{-1}, τ (CF_3·CO_2H) 5·3 (2H, m), 6·8 (4H, m), and 7·8 (6H, s) (Found: C, 41·5; H, 4·8; N, 10·9; S, 12·4. $C_9H_{12}N_2O_5S$ requires C, 41·5; H, 4·65; N, 10·8; S, 12·3%).

1-*Acetylhexahydrothieno*[3,4-d]*imidazol*-2-*one* SS-*Dioxide* (2; $R^1 =$ H, $R^2 =$ Ac).—Hexahydrothieno[3,4-*d*]imidazol-2-one 5,5-dioxide (214 mg) was boiled under reflux with acetyl chloride (5 ml) in acetic acid (7·5 ml) for 30 min to give a mixture of mono- and di-acetyl compounds. The less soluble *monoacetyl derivative* was isolated by crystallising the mixture from water; m.p. 260—262°, $\nu_{max.}$ 3280, 1740, 1660, 1320, and 1170 cm^{-1}, τ (CF_3·CO_2H) 5·3 (2H, m), 6·8 (4H, m), and 7·8 (3H, s) (Found: C, 38·5; H, 4·5; N, 12·6; S, 14·8. $C_7H_{10}N_2O_4S$ requires C, 38·55; H, 4·6; N, 12·8; S, 14·7%).

Both acetyl derivatives were deacetylated by brief boiling with base.

4-*Hydroxyaminotetrahydro*-3-*thienylurea* SS-*Dioxide* (22).—2,3-Dihydro-3-thienylurea *SS*-dioxide (528 mg), hydroxylamine hydrochloride (417 mg), and water were stirred together, and a solution of sodium hydrogen carbonate (510 mg) in water (10 ml) was added during 2 min. The mixture was stirred at 60° for 2 h to give a clear solution, which was evaporated to dryness. The residue was crystallised from water to give the *hydroxylamine derivative* (464 mg, 75%), m.p. 185—186° (from 1 : 1 water–ethanol), $\nu_{max.}$ 3440, 3390, 3270, 1655, 1610, 1540, 1305, and 1130 cm^{-1}, τ (CF_3·CO_2H) 3·7br (1H), 5·1—6·0 (2H, m), and 6·3—7·1 (4H, m) (Found: C, 29·1; H, 5·45; N, 20·05; S, 12·3. $C_5H_{11}N_3O_4S$ requires C, 28·7; H, 5·3; N, 20·1; S, 15·3%).

6-*Bromohexahydrothieno*[3,4-d]*oxazol*-2-*imine* 5,5-*Dioxide Hydrobromide* (23).—2,3-Dihydro-3-thienylurea *SS*-dioxide (540 mg) was stirred in acetic acid (25 ml) at 65° with bromine. After 2 h the solid was filtered off and washed with ethanol and ether. Evaporation of the mother liquors and addition of ethanol produced more of the *salt* (990 mg, 96%), m.p. 190—192° (from 15% water–ethanol), $\nu_{max.}$ 3200, 1705, 1530, 1325, and 1115 cm^{-1}, τ(CF_3·CO_2H) 4·5br (1H, d, J 10 Hz), 5·1 (1H, m), 5·2br (1H, s), and 6·7 (2H, m) (Found: C, 18·0; H, 2·65; Br, 46·8; N, 8·2; S, 9·8. $C_5H_8N_2Br_2O_3S$ requires C, 17·9; H, 2·4; Br, 47·6; N, 8·3; S, 9·6%).

5-*Bromo*-2,3-*dihydro*-3-*thienylurea* (25).—The bromothieno-oxazole (23) hydrobromide (336 mg) was stirred in water (2 ml) and 0·2N-sodium hydroxide solution (5 ml) was added slowly to precipitate a white solid. The volume of solution was reduced by half and the urea (631 mg, 86%) was filtered off; m.p. 222—224° (from water), $\nu_{max.}$ 3470, 3380, 3270, 3100, 1660, 1560, 1310, and 1150 cm^{-1}, τ(CF_3·CO_2H) 1·7br (2H, s), 3·4 (1H, d, J 3 Hz), 3·4br (1H), 5·0 (1H, m), and 6·0—7·0 (2H, dq, J_{AB} 14, J_{AX} 7, J_{BX} 4 Hz) (Found: C, 23·8; H, 2·95; Br, 30·95; N, 10·85; S, 12·85. $C_5H_7N_2BrO_3S$ requires C, 23·55; H, 2·8; Br, 31·3; N, 11·0; S, 12·6%).

5-*Bromo*-4-*hydroxyaminotetrahydro*-3-*thienylurea* SS-*Dioxide* (26).—5-Bromo-2,3-dihydro-3-thienylurea *SS*-dioxide (105 mg), hydroxylamine sulphate (134 mg), and sodium hydrogen carbonate (140 mg) were stirred together in water (10 ml) at 65° for 4 h. The solution was evaporated to dryness and the residue extracted with hot methanol. Evaporation of the extract gave a solid which crystallised from 20% water–methanol to give the *hydroxylamine*

derivative, m.p. 189—190°, $\nu_{max.}$ 3490, 3390, 3240, 1660, 1560, 1315, and 1125 cm^{-1}, τ(CF_3·CO_2H) 3·8br (1H), 4·9 (1H, d, *J* 9 Hz), 5·3 (1H, m), 5·9 (1H, m), and 6·1—7·0 (2H, dq) (Found: C, 21·2; H, 3·8; Br, 27·85; N, 14·7; S, 11·0. $C_5H_{10}BrN_3SO_4$ requires C, 20·85; H, 3·5; Br, 27·75; N, 14·6; S, 11·1%).

N-(2,3-*Dihydro*-3-*thienyl*)-NN′-*diphenylurea* SS-*Dioxide* (20; $R^1 = R^2 =$ Ph).—3-Anilino-2,3-dihydrothiophen 1,1-dioxide (32 mg) and phenyl isocyanate (0·5 ml) were heated until all the solid had dissolved. The mixture was cooled and triturated with hot petroleum to remove the excess of isocyanate. The residue was dissolved in a few drops of benzene and added to briskly stirred light petroleum (15 ml). The solid was collected and the *urea* (43·2 mg, 86%) crystallised from toluene; m.p. 132—134°, $\nu_{max.}$ 3400, 1670, 1600, 1510, 1300, and 1110 cm^{-1}, τ($CDCl_3$–D_2O) 2·3—3·0 (10H, m), 3·3 (2H, m), 3·9 (1H, m), and 6·0—6·9 (2H, dq, J_{AB} 14, J_{AX} 8, J_{BX} 4 Hz) (Found: C, 62·3; H, 5·0; N, 8·5; S, 10·0. $C_{17}H_{16}N_2O_3S$ requires C, 62·2; H, 4·9; N, 8·5; S, 9·8%).

cis-*Hexahydro*-1,3-*diphenylthieno*[3,4-d]*imidazol*-2-*one* 5,5-*Dioxide* (2; $R^1 = R^2 =$ Ph).—The foregoing urea (67 mg) was stirred at room temperature for 4 h with 0·5N-sodium ethoxide in ethanol (10 ml). The solution was evaporated to dryness, water was added, and the product was extracted with chloroform. Evaporation yielded the *cyclic urea* (65·5 mg), m.p. 176—177° (from methanol), $\nu_{max.}$ 1695, 1600, 1500, 1295, and 1160 cm^{-1}, τ (CF_3·CO_2H) 2·9br (10H, s), 4·9br (2H, s), and 6·9br (4H, s) (Found: C, 62·0; H, 5·0; N, 8·4; S, 9·7. $C_{17}H_{16}N_2O_3S$ requires C, 62·2; H, 4·9; N, 8·5; S, 9·8%).

Hexahydro-1,3-*dimethylthieno*[3,4-d]*imidazol*-2-*one* 5,5-*Dioxide* (2; $R^1 = R^2 =$ Me).—4-Bromotetrahydro-3-thienylmethylcarbamate *SS*-dioxide (99 mg) was heated under reflux with triethylamine (67 mg) in ethanol (5 ml) for 24 h. The solvent was evaporated off, water was added to the residue, and the mixture was extracted with chloroform. Evaporation yielded an oil (46 mg, 85%) identified as 3-methylamino-2,3-dihydrothiophen 1,1-dioxide (treatment with ethoxide isomerised the oil to 2,3-dihydro-4-methylaminothiophen 1,1-dioxide), $\nu_{max.}$ (film) 3350, 1300, and 1140 cm^{-1}, τ 3·2 (2H, s and d, *J* 2 Hz), 5·8 (1H, m), 6·3—7·2 (2H, dq, J_{AB} 14, J_{AX} 7, J_{BX} 4 Hz), and 7·6 (3H, s).

The crude oil (46 mg) was heated under reflux with methyl isocyanate (0·5 ml) for 30 min. The excess of reagent was evaporated off and the residue triturated with light petroleum and then extracted with hot benzene. Evaporation yielded an oil (45 mg) identified as *N*-(2,3-dihydro-3-thienyl)-*NN*′-dimethyl urea, $\nu_{max.}$ (film) 3400, 1640, 1540, 1300, and 1140 cm^{-1}, τ 3·2 (2H, m), 4·1 (1H, m), 4·8 (1H, m, NH), 6·2—7·2 (2H, dq, J_{AB} 14, J_{AX} 8, J_{BX} 4 Hz), and 7·2 (6H).

The urea (72 mg) was stirred with 0·5N-sodium ethoxide in ethanol (5 ml) at room temperature overnight. The solvent was evaporated off, water was added to the residue, and the product was extracted with chloroform. Evaporation yielded the *cyclic urea*, m.p. 178—179° (from ethanol), $\nu_{max.}$ 1690, 1510, 1320, and 1120 cm^{-1}, τ 5·6br (2H, m), 6·7br (4H, m), and 7·1 (6H, s) (Found: C, 41·2; H, 5·9; N, 13·95; S, 15·7. $C_7H_{12}N_2O_3S$ requires C, 41·2; H, 5·9; N, 13·7; S, 15·7%).

N-(2,3-*Dihydro*-3-*thienyl*)-N′-*methyl*-N-*phenylurea* (20; $R^1 =$ Ph, $R^2 =$ Me).—3-Anilino-2,3-dihydrothiophen 1,1-dioxide (232 mg) was heated under reflux with methyl isocyanate (1 ml) for 5 h. The excess of reagent was evaporated off and the residue washed with hot light petroleum to give the *urea* (171 mg, 85%), m.p. 172—174° (from ethanol), $\nu_{max.}$ 3400, 1655, 1600, 1520, 1300, and 1140 cm^{-1}, τ ($CDCl_3$–CF_3·CO_2H) 2·5 (5H, m), 3·3 (1H, m), 4·0 (1H, m), 5·9—6·8 (2H, dq, J_{AB} 14, J_{AX} 7, J_{BX} 4 Hz), 6·4br (1H), and 7·2 (3H, s) (Found: C, 54·0; H, 5·1; N, 10·4; S, 12·0. $C_{12}H_{14}N_2O_3S$ requires C, 54·1; H, 5·3; N, 10·5; S, 12·0%).

Hexahydro-1-*methyl*-3-*phenylthieno*[3,4-d]*imidazol*-2-*one* 5,5-*Dioxide* (2; $R^1 =$ Ph, $R^2 =$ Me).—The foregoing urea (84 mg) was stirred with 0·5N-sodium ethoxide in ethanol (5 ml) at room temperature overnight. The suspension was evaporated to dryness, water was added, and the product was extracted with chloroform. Evaporation gave the *cyclic urea*, m.p. 191—192° (from 5% water–ethanol), $\nu_{max.}$ 1695, 1600, 1510, 1315, and 1120 cm^{-1}, τ(CF_3·CO_2H) 3·0 (5H, m), 4·8—5·2 (1H, m), 5·2—5·6 (1H, m), and 6·4—7·0 (3H, s) (Found: C, 54·1; H, 5·1; N, 10·4; S, 12·25. $C_{12}H_{14}N_1O_3S$ requires C, 54·1; H, 5·3; N, 10·5; S, 12·0%).

Perhydro-1,3,5-*trimethyl*-s-*triazine*-2-*spiro*-3′-*thiophen*-4,6-*dione* SS-*Dioxide* (27).—Sodium hydride (50% oil dispersion; 85 mg) was washed with dry ether. Dry dioxan (10 ml) and 2,3-dihydro-4-methylaminothiophen 1,1-dioxide (251 mg) were added. The mixture was heated under reflux for 3 h and cooled, and methyl isocyanate (0·5 ml) was added. After stirring for 24 h at room temperature a few drops of water were added and the mixture was evaporated to dryness. The residue was taken up in water and extracted with chloroform. Evaporation yielded the *spiro-compound*, m.p. 179—180° (from 1 : 1 ethanol–chloroform), $\nu_{max.}$ 1700, 1660, 1305, and 1190 cm^{-1}, τ(CF_3·CO_2H) 6·5 (2H, s), 6·8 (2H, t), 7·2 (9H, s), and 7·4 (2H, t) (Found: C, 41·4; H, 5·7; N, 16·2; S, 12·25. $C_9H_{15}N_3O_4S$ requires C, 41·4; H, 5·8; N, 16·1; S, 12·3%).

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