Rearrangement of 4-Oxothiochroman-1-io(bismethoxycarbonyl)methanides to Tetrahydro-1-benzothiepin-5-ones

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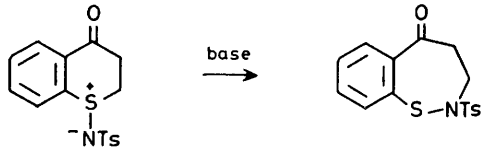
Heating thiochroman-4-ones with dimethyl diazomalonate without solvent or in refluxing toluene in the presence of copper(II) sulphate gave the corresponding bismethoxycarbonylmethanides (4) and dimethyl 5-oxo-2,3,4,5-tetrahydro-1-benzothiepin-2,2-dicarboxylates (5). Treatment of the sulphonium methanides (4) with triethylamine afforded (5).

RECENTLY we have described a novel rearrangement of 1-*p*-tolylsulphonyliminothiochroman-4-ones (1) into tetrahydro-1,2-benzothiazepin-5-ones (2).[1] We have now found that the isoelectronic sulphonium methanides (4) undergo a similar base-catalysed rearrangement to give tetrahydro-1-benzothiepin-5-ones (5).[2]

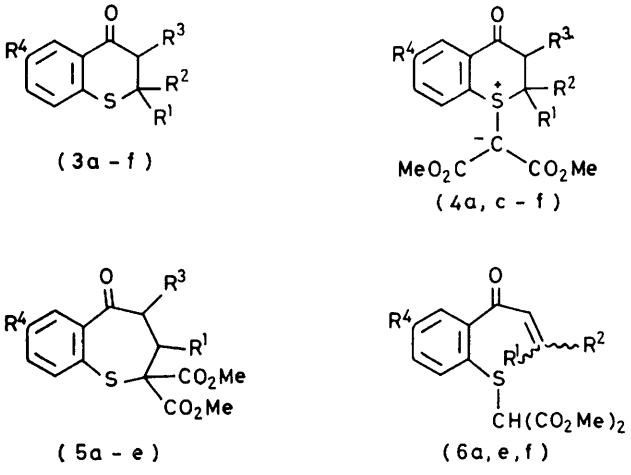


(1) (2)

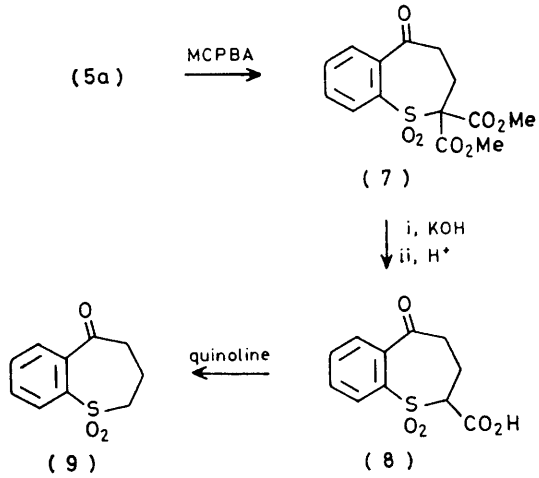
SCHEME 1

According to Ando's procedure,[3] the reaction of thiochroman-4-one (3a) with dimethyl diazomalonate in the presence of anhydrous copper(II) sulphate at 100—110 °C for 5 h (procedure A) gave a mixture of the bismethoxycarbonylmethanide (4a) (minor) and tetrahydro-1-benzothiepin-5-one (5a)[4] (major). Since the products from this reaction could not be separated, the whole mixture was treated with triethylamine in chloroform at room temperature to afford (5a) in 68% overall yield. The structure of (5a) was established by a combination of spectral and chemical evidence. Its i.r. spectrum showed two carbonyl absorptions at 1 720 (ester carbonyl) and 1 670 (aromatic ketone) cm^{-1} and the n.m.r. spectrum revealed two multiplets (2 H each) at δ 2.4—2.7 and 2.8—3.0, a singlet (6 H) at δ 3.80, and a multiplet (4 H) in the aromatic region between δ 7.3 and 7.8. Oxidation of (5a) with *m*-chloroperoxybenzoic acid (MCPBA) gave the sulphone (7). Alkaline hydrolysis of (7) followed by decarboxylation of the resulting monocarboxylic acid (8) gave known 5-oxotetrahydro-1-benzothiepin 1,1-dioxide (9).[5]

The reaction of (3b) and (3c) with dimethyl diazomalonate again gave an inseparable mixture of (4b, c) and (5b, c) which was treated with triethylamine to afford (5b, c) in 75 and 86% yields, respectively. However, the 3-methyl derivative (3d) afforded only the bismethoxycarbonylmethanide (4d) in 70% yield under the same reaction conditions (without base treatment). The bismethoxycarbonylmethanides (4a, c) could be isolated in 68 and 75% yields, respectively, by crystallisation of the crude products obtained from the reaction of (3a, c) with dimethyl diazomalonate in refluxing toluene[6] in the presence of copper(II) sulphate (procedure B). Using the procedure B the bismethoxycarbonylmethanides (4e, f) were obtained from (3e, f) in 64



a; $R^1 = R^2 = R^3 = R^4 = H$
b; $R^1 = R^2 = R^3 = H$, $R^4 = Me$
c; $R^1 = R^2 = R^3 = H$, $R^4 = Cl$
d; $R^1 = R^2 = R^4 = H$, $R^3 = Me$
e; $R^1 = Me$, $R^2 = R^3 = R^4 = H$
f; $R^1 = R^2 = Me$, $R^3 = R^4 = H$

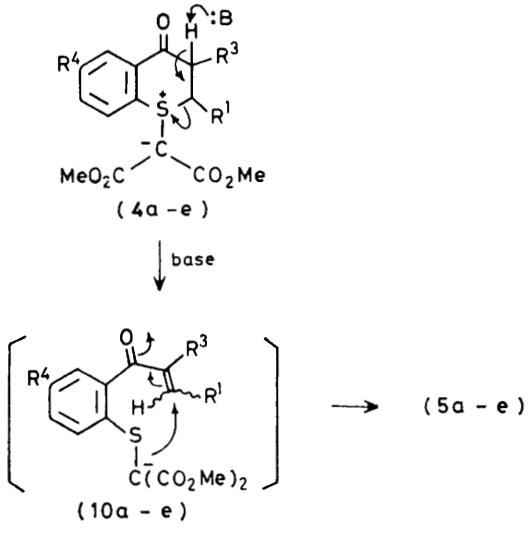


SCHEME 2

and 47% yields, respectively. The structure of (4a, c—f) was assigned on the basis of the spectroscopic evidence (see Experimental section).

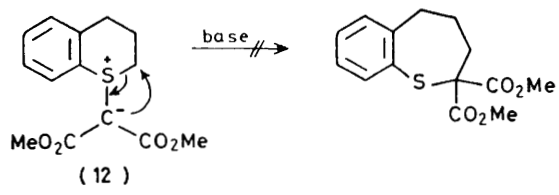
When a chloroform solution of (4a, c, d) was treated with triethylamine at room temperature for 30 min, a nearly quantitative yield of (5a, c, d) was obtained. This reaction is affected by the nature of the substituent(s), particularly at the 2-position, and the reaction conditions (solvent, base or acid). Thus, treatment of the 2-methyl derivative (4e) with triethylamine in chloroform for a short time (5 min) gave an inseparable mixture of (5e) and (6e) in a ratio of 1 : 8 (by n.m.r. spectroscopy). If the same reaction mixture was allowed to stand for 16 h at room temperature, the sole isolable product was (5e). This cyclisation proceeded much more rapidly in acetonitrile (it was complete within 1 h). The reaction of the 2,2-dimethyl congener (4f) with triethylamine resulted in the formation of an oily ring-opened product (6f) in 86% yield. Further treatment of (6f) with triethylamine in chloroform or acetonitrile did not give the cyclised product.

The base-induced rearrangement of the ylides (4a—e) to (5a–e) * can best be rationalised in terms of the intermediacy of (10a—e) which may arise by β-elimination from (4a—e). An intramolecular Michael addition leads to the observed products (5a—e). The second step



Scheme 3

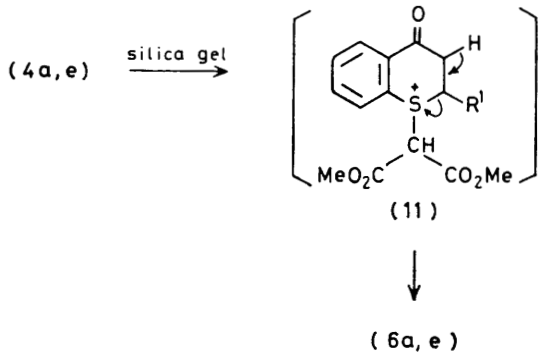
* An alternative mechanism for the formation of (5a—e) would involve a Stevens-type rearrangement. This possibility, however, was eliminated by the fact that thiochroman-1-io(bismethoxycarbonyl)methanide (12) [7] was recovered unchanged under the reaction conditions used for the rearrangement of (4a).



Scheme 5

appears to be affected by the steric effect of the methyl substituent(s) at the β-position of the enone system, as shown in the case of (4f) which gave no cyclised product. In the mechanistic details the base-catalysed rearrangement of (4) parallels closely the behaviour of 1-*p*-tolylsulphonyliminothiochroman-4-one (1).[1]

The ring opening of (4) is also promoted by silica gel. Thus, when a mixture of (4a) and silica gel in chloroform was stirred at room temperature for 1 h, the ring-opened product (6a) was quantitatively obtained. The n.m.r. spectrum of (6a) revealed two singlets (3 H each, 2 × OCH_3) at δ 3.72 and 3.75, a singlet (1 H, SCH) at δ 4.28, three doublets of doublets (1 H each, $COCH{=}CH_2$) at δ 5.22, 5.47, and 6.14, and a multiplet (4 H) in the aromatic region. Similarly (4e) gave pure (6e). Presumably, the protonated intermediate (11) would be involved in this reaction. Treatment of the ring-opened products (6a) and (6e) with triethylamine in chloroform or acetonitrile gave (5a, e) in quantitative yield. However, the precise mechanism for the direct formation of (5a—c) from (3a—c) without the use of base or acid is uncertain.



Scheme 4

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 JASCO IRA-1 spectrophotometer. Low- and high-resolution mass spectra were obtained with a JMS-D-300 instrument at 70 eV.

Materials.—Thiochroman-4-one (3a),[8] and 6-methyl- (3b),[8] 6-chloro- (3c),[9] 3-methyl- (3d),[10] 2-methyl- (3e),[9,10] and 2,2-dimethyl-thiochroman-4-ones (3f) [9] were synthesised as described in the literature.

Reaction of (3a) *with Dimethyl Diazomalonate.*—(A) According to the procedure reported by Ando *et al.*,[3] a mixture of (3a) (500 mg, 3.1 mmol), dimethyl diazomalonate (700 mg, 4.5 mmol), and anhydrous copper(II) sulphate (100 mg) was heated at 100—110 °C for 5 h with vigorous stirring. After cooling, the mixture was diluted with $CHCl_3$ (20 ml) and filtered. To the filtrate was added triethylamine (0.1 ml) and the mixture was allowed to stand at room temperature for 5 min. The reaction mixture was washed with 10% hydrochloric acid and water, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel (benzene–AcOEt) to give *dimethyl 5-oxo-2,3,4,5-tetrahydro-1-benzothiepin-2,2-dicarboxylate* (5a) (611 mg, 68%), m.p. 79—80 °C (from ethanol) (Found: C,

56.75; H, 4.75. $C_{14}H_{14}O_5S$ requires C, 57.13; H, 4.79%); $\nu_{max.}$ (KCl) 1 720 (C=O) and 1 670 (C=O) cm^{-1}; δ ($CDCl_3$) 2.4—2.7 (2 H, m), 2.8—3.0 (2 H, m), 3.80 (6 H, s, 2 × OCH_3), and 7.3—7.8 (4 H, m, aromatic).

(B) A mixture of (3a) (600 mg, 3.7 mmol), dimethyl diazomalonate (720 mg, 4.6 mmol), and anhydrous copper(II) sulphate (100 mg) in anhydrous toluene (1 ml) was heated at 105 °C under nitrogen atmosphere for 1 h with vigorous stirring. After cooling, the reaction mixture was diluted with $CHCl_3$ (20 ml) and filtered. The filtrate was washed with water, dried (Na_2SO_4), and concentrated to give a brown oil which, upon addition of AcOEt and n-hexane, crystallised. The crystals were collected by filtration and recrystallised from acetone to give *4-oxothiochroman-1-io(bismethoxycarbonyl)methanide* (**4a**) (720 mg, 67%), m.p. 125—126 °C * (Found: C, 56.95; H, 4.7. $C_{14}H_{14}O_5S$ requires C, 57.13; H, 4.79%); $\nu_{max.}$ (KCl) 1 670 (C=O) and 1 630 (C=O) cm^{-1}; δ ($CDCl_3$) 3.1—3.5 (3 H, m), 3.67 (6 H, s, 2 × OCH_3), 4.7—5.2 (1 H, m), 7.4—7.7 (3 H, m, aromatic), and 8.1—8.3 (1 H, m, aromatic); *m/e* 294 (90%, M^+), 262 (33), 235 (32), 218 (72), 175 (70), 163 (100), 150 (94), and 147 (85). The filtrate was concentrated and submitted to column chromatography on silica gel (AcOEt) to give (5a) (50 mg, 5%).

Reaction of (3b) *with Dimethyl Diazomalonate*.—Using procedures (A) and (B), two products were obtained from (3b) (400 mg). Because the products could not be separated, the whole mixture was dissolved in $CHCl_3$ (10 ml) containing triethylamine (0.1 ml) and the solution was stirred at room temperature for 30 min. The mixture was washed with 10% hydrochloric acid and water, dried (Na_2SO_4), and concentrated to give *dimethyl 7-methyl-5-oxo-2,3,4,5-tetrahydro-1-benzothiepin-2,2-dicarboxylate* (5b) [(A) 520 mg, 75%, and (B) 430 mg, 62%], m.p. 111—113 °C (from n-hexane–ethanol) (Found: C, 58.1; H, 5.15. $C_{15}H_{16}O_5S$ requires C, 58.43; H, 5.32%); $\nu_{max.}$ (KCl) 1 720 (C=O) and 1 670 (C=O) cm^{-1}; δ ($CDCl_3$) 2.2—3.0 (4 H, m), 2.40 (3 H, s, CH_3), 3.78 (6 H, s, 2 × OCH_3), and 7.1—7.5 (3 H, m, aromatic).

Reaction of (3c) *with Dimethyl Diazomalonate*.—Using procedure (A), *dimethyl 7-chloro-5-oxo-2,3,4,5-tetrahydro-1-benzothiepin-2,2-dicarboxylate* (5c) (230 mg, 86%) was obtained from (3c) (200 mg). Compound (5c) had m.p. 127—128 °C (from ethanol) (Found: C, 50.9; H, 4.2. $C_{14}H_{13}ClO_5S$ requires C, 51.15; H, 3.99%); $\nu_{max.}$ (KCl) 1 720 (C=O) and 1 680 (C=O) cm^{-1}; δ ($CDCl_3$) 2.3—3.0 (4 H, m), 3.79 (6 H, s, 2 × OCH_3), and 7.3—7.7 (3 H, m, aromatic). Using the procedure (B), *6-chloro-4-oxothiochroman-1-io(bismethoxycarbonyl)methanide* (**4c**) (620 mg, 75%) was obtained as the sole isolable product from (3c) (500 mg). Compound (4c) had m.p. 139—149 °C (from acetone) (Found: C, 51.35; H, 4.15. $C_{14}H_{13}ClO_5S$ requires C, 51.15; 3.99%); $\nu_{max.}$ (KCl) 1 680 (C=O) and 1 630 (C=O) cm^{-1}; δ ($CDCl_3$) 3.05—3.5 (3 H, m), 3.68 (6 H, s, 2 × OCH_3), 4.7—5.35 (1 H, m), 7.55 (2 H, m, aromatic), and 8.14 (1 H, m, aromatic); *m/e* 328 (100%, M^+), 296 (8), 269 (49), 252 (15), 209 (49), 197 (15), 184 (80), and 181 (36).

Reaction of (3d) *with Dimethyl Diazomalonate*.—Using the procedure (A) without treatment with base, *3-methyl-4-oxothiochroman-1-io(bismethoxycarbonyl)methanide* (**4d**) (323 mg, 70%) was obtained from (3d) (267 mg). Compound (4d) had m.p. 157.5—159 °C (from AcOEt) (Found: C, 58.25; H, 5.1. $C_{15}H_{16}O_5S$ requires C, 58.43; H, 5.23%); $\nu_{max.}$ ($CHCl_3$) 1 680 (C=O) and 1 640 (C=O) cm^{-1}; δ ($CDCl_3$) 1.44 (3 H, d, *J* 7 Hz, 3-CH_3), 3.0—3.5 (2 H, m), 3.67 (6 H, s, 2 × OCH_3), 4.78 (1 H, dd, *J* 15 and 11 Hz), 7.5—7.7 (3 H, m, aromatic), and 8.1—8.3 (1 H, m, aromatic); *m/e* 308 (15%, M^+), 276 (3), 249 (4), 232 (9), 217 (20), 189 (16), 177 (73), 164 (100).

Reaction of (3e) *with Dimethyl Diazomalonate*.—Using procedure (B), *2-methyl-4-oxothiochroman-1-io(bismethoxycarbonyl)methanide* (**4e**) (550 mg, 64%) and *dimethyl 3-methyl-5-oxo-2,3,4,5-tetrahydro-1-benzothiepin-2,2-dicarboxylate* (**5e**) (162 mg, 12%) were obtained from (3e) (500 mg). Compound (4e) had m.p. 109—111 °C (from AcOEt–n-hexane) (Found: C, 58.15; H, 5.2. $C_{15}H_{16}O_5S$ requires C, 58.43; H, 5.23%); $\nu_{max.}$ (KCl) 1 670 (C=O) and 1 640 (C=O) cm^{-1}; δ ($CDCl_3$) 1.54 (3 H, d, *J* 6 Hz, 2-CH_3), 2.8—3.45 (2 H, m), 3.68 (6 H, s, 2 × OCH_3), 4.75—5.2 (1 H, m), 7.4—7.7 (3 H, m, aromatic), and 8.05—8.25 (1 H, m, aromatic); *m/e* 308 (20%, M^+), 232 (63), 189 (38), and 177 (100). Compound (5e) had m.p. 90—91 °C (from ethanol) (Found: C, 58.2; H, 5.2. $C_{15}H_{16}O_5S$ requires C, 58.43; H, 5.23%); $\nu_{max.}$ (KCl) 1 720 (C=O) and 1 670 (C=O) cm^{-1}; δ ($CDCl_3$) 1.09 (3 H, d, *J* 6 Hz, 3-CH_3), 2.6—3.6 (4 H, m), 3.40 and 4.80 (3 H each, both s, 2 × OCH_3), and 7.1—8.05 (4 H, m, aromatic).

Reaction of (3f) *with Dimethyl Diazomalonate*.—Using procedure (B), *2,2-dimethyl-4-oxothiochroman-1-io(bismethoxycarbonyl)methanide* (**4f**) (390 mg, 47%) and *dimethyl (2-β-methylcrotonoylphenyl)thiomalonate* (**6f**) (100 mg, 12%) were obtained from (3f) (500 mg). Compound (4f) had m.p. 158—160 °C (from AcOEt) (Found: C, 59.4; H, 5.5. $C_{16}H_{18}O_5S$ requires C, 59.61; H, 5.63%); $\nu_{max.}$ (KCl) 1 670 (C=O) and 1 650 (C=O) cm^{-1}; δ ($CDCl_3$) 1.51 and 1.58 [3 H each, s each, 2-$(CH_3)_2$], 2.80 and 3.83 (1 H each, ABq, *J* 17 Hz, H-3), 3.47 and 3.74 (3 H each, both br s, 2 × OCH_3), and 7.5—8.35 (1 H, m, aromatic); *m/e* 322 (10%, M^+), 267 (35), 246 (24), 207 (93), and 191 (100). Compound (6f) was a yellowish oil (Found: M^+, 322.0875. $C_{16}H_{18}O_5S$ requires *M*, 322.0875); $\nu_{max.}$ ($CHCl_3$) 1 730 (C=O) and 1 650 (C=O) cm^{-1}; δ ($CDCl_3$) 1.70 and 1.98 (total 3 H, 1 : 5,† both d, *J* 2 Hz, CH_3), 1.89 and 2.17 (total 3 H, 1 : 5,† both d, *J* 2 Hz, CH_3), 3.71 (6 H, s, 2 × OCH_3), 4.70 [1 H, s, C*H*-$(CO_2Me)_2$], 6.41 (1 H, m, vinylic), and 7.0—7.6 (4 H, m, aromatic).

Reactions of the Biscarbomethoxymethylides (4a, c—f).—(a) *Reaction of* (4a, c—f) *in the presence of triethylamine in* $CHCl_3$. A solution of (4a) (100 mg, 0.33 mmol) in $CHCl_3$ (5 ml) containing triethylamine (0.1 ml) was stirred at room temperature for 30 min. The solution was washed with 10% hydrochloric acid and water, dried (Na_2SO_4), and concentrated to give a solid, which was recrystallised from ethanol giving (5a) (98 mg, 98%). In this manner, (4c) (50 mg) and (4d) (100 mg) gave (5c) (46 mg, 92%) and *dimethyl 4-methyl-5-oxo-2,3,4,5-tetrahydro-1-benzothiepin-2,2-dicarboxylate* (5d) (91 mg, 91%), respectively. Compound (5d) was an oil, $\nu_{max.}$ ($CHCl_3$) 1 730 (C=O) and 1 680 (C=O) cm^{-1}; δ ($CDCl_3$) 1.35 (3 H, d, *J* 7 Hz, 4-CH_3), 2.2—2.7 (2 H, m), 2.85—3.2 (1 H, m), 3.68 and 3.82 (3 H each, both s, 2 × OCH_3), and 7.1—7.7 (4 H, m, aromatic); *m/e* 308 (M^+). It formed the 2,4-dinitrophenylhydrazone, m.p. 257—260 °C (from methanol–$CHCl_3$) (Found: C, 52.0; H, 4.1; N, 11.55.

* The melting point (m.p. 142—143 °C) reported in ref. 2 should be revised.

† The splitting patterns of the methyl signals are dependent upon the temperature and the solvent. Thus, the ratio of the splitting signals became *ca.* 1 : 1 in $(CD_3)_2SO$. The two higher signals disappeared at *ca.* 100 °C in $(CD_3)_2SO$ and reappeared after standing for 1 day. The reason for this splitting is uncertain at the present time. A similar splitting was observed with (6e) (*vide infra*).

$C_{21}H_{20}N_4O_8S$ requires C, 51.65; H, 4.13; N, 11.47%). Compound (4e) (100 mg) was treated with triethylamine for 5 min and work-up as described above gave an oily residue. The residue was purified by passing through a short silica gel column [benzene–AcOEt (10 : 1)] to give a pale yellow oil (99 mg, 99%), which consisted of two products, (5e) and *dimethyl* (2-*crotonoylphenyl*)*thiomalonate* (6e), in a ratio of 1 : 8 (n.m.r.). Spectral data for pure (6e) are given below. When the solution of (4e) in chloroform containing triethylamine was allowed to stand for 16 h at room temperature, the sole isolable product was (5e). Treatment of (4f) (310 mg) with triethylamine in chloroform for 30 min gave (6f) (300 mg, 96%). Compound (12) [7] did not react under these conditions.

(b) *Reaction of* (4e) *in the presence of triethylamine in acetonitrile*. A solution of (4e) (95 mg, 0.3 mmol) in acetonitrile (5 ml) containing triethylamine (0.1 ml) was stirred at room temperature for 1 h, concentrated, and diluted with chloroform (20 ml). The solution was washed with 10% hydrochloric acid and water, dried (Na_2SO_4), and concentrated to give (5e) (90 mg, 95%).

(c) *Reaction of* (4a, e) *in the presence of silica gel in* $CHCl_3$. A mixture of (4a) (50 mg) and silica gel (200 mg) in $CHCl_3$ (5 ml) was stirred at room temperature for 1 h. The mixture was filtered and concentrated to give *dimethyl* (2-*acryloylphenyl*)*thiomalonate* (6a) (50 mg, 100%) as an oil (Found: M^+, 294.0551. $C_{14}H_{14}O_5S$ requires M, 294.0559), $\nu_{max.}$ ($CHCl_3$) 1 720 (C=O) cm^{-1}; δ ($CDCl_3$) 3.72 and 3.75 (3 H each, both s, 2 × OCH_3), 4.28 (1 H, s, SCH), 5.22 (1 H, dd, J 10 and 2 Hz, vinylic), 5.47 (1 H, dd, J 17 and 2 Hz, vinylic), 6.14 (1 H, dd, J 10 and 17 Hz, vinylic), and 6.9—7.7 (4 H, m, aromatic). Compound (6a) was converted quantitatively into (5a) by treating with triethylamine in $CHCl_3$. Similarly (4e) gave (6e) as an oil (Found: M^+, 308.0723. $C_{15}H_{16}O_5S$ requires M, 308.0718). $\nu_{max.}$ ($CHCl_3$) 1 720 (C=O) cm^{-1}; δ ($CDCl_3$) 1.71 and 1.97 (total 3 H, *ca.* 3 : 1, both d, J 5 Hz, CH_3), 3.73 and 3.77 (3 H each, both s, 2 × OCH_3), 4.33 (1 H, s, SCH), 5.79 (2 H, m, vinylic), and 6.95—7.7 (4 H, m, aromatic). This compound was also converted into (5e) by treating with triethylamine.

2,2-*Bismethoxycarbonyl*-5-*oxo*-2,3,4,5-*tetrahydro*-1-*benzothiepin* 1,1-*Dioxide* (7).—To an ice-cooled solution of (5a) (500 mg, 1.7 mmol) in $CHCl_3$ (15 ml) was added *m*-chloroperbenzoic acid (760 mg, 4.4 mmol) with vigorous stirring. The mixture was stirred at room temperature for 1 day. The reaction mixture was washed with saturated $NaHCO_3$ solution and water, dried (Na_2SO_4), and concentrated to give white crystals, which were recrystallised from ethanol giving (7) (540 mg, 98%), m.p. 108—109 °C (from ethanol) (Found: C, 51.4; H, 4.25. $C_{14}H_{14}O_7S$ requires C, 51.53; H, 4.32%); $\nu_{max.}$ (KCl) 1 740 (C=O), 1 690 (C=O), 1 330 and 1 150 (SO_2) cm^{-1}; δ ($CDCl_3$) 2.4—2.6 (2 H, m), 2.85—3.15 (2 H, m), 3.82 (6 H, s, 2 × OCH_3), and 7.5—8.1 (4 H, m, aromatic).

2-*Carboxy*-5-*oxo*-2,3,4,5-*tetrahydro*-1-*benzothiepin* 1,1-*Dioxide* (8).—A solution of (7) (200 mg, 0.6 mmol) and potassium hydroxide (210 mg) in 80% methanol (10 ml) was heated at 75—85 °C for 1 h. After cooling, the mixture was acidified with concentrated hydrochloric acid and extracted with AcOEt. The extract was washed with water, dried (Na_2SO_4), and concentrated to give white crystals of (8) (120 mg, 77%), m.p. 167—168 °C (from n-hexane–benzene) (Found: C, 51.8; H, 3.9. $C_{11}H_{10}O_5S$ requires C, 51.96; H, 3.96%); $\nu_{max.}$ (KCl) 1 710 (CO_2H), 1 680 (C=O), 1 330, and 1 140 (SO_2) cm^{-1}; δ (CD_3OD) 2.0—2.5 (2 H, m), 2.85—3.2 (2 H, m), 4.1—4.6 (1 H, m), and 7.45—8.05 (4 H, m, aromatic).

5-*Oxo*-2,3,4,5-*tetrahydro*-1-*benzothiepin* 1,1-*Dioxide* (9).—A solution of (8) (120 mg, 0.47 mmol) in quinoline (5 ml) was heated at 120 °C for 2 h. The mixture was diluted with $CHCl_3$ (20 ml) and washed with 10% hydrochloric acid and water, dried (Na_2SO_4), and concentrated to give a solid which was recrystallised from ethanol giving (9) (55 mg, 55%), m.p. 155—156 °C (lit.,[6] 155—156 °C) (from ethanol); $\nu_{max.}$ (KCl) 1 680 (C=O), 1 300, and 1 150 (SO_2) cm^{-1}; δ ($CDCl_3$) 2.0—2.4 (2 H, m), 2.95—3.2 (2 H, m), 3.3—3.6 (2 H, m), and 7.55—8.1 (4 H, m, aromatic).

[1/625 *Received*, 22*nd April*, 1981]

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