Studies Related to Penicillins. Part 18.[1] Epimerisations of Benzylpenicillin Sulphones [2]

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In the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), methyl benzylpenicillinate 1,1-dioxide (9) equilibrates with methyl benzyl-6-epipenicillinate 1,1-dioxide (10). Under corresponding conditions, methyl benzyl-5-epipenicillinate 1,1-dioxide (11) forms a mixture of methyl benzyl-3,5,6-triepipenicillinate 1,1-dioxide (12), methyl benzyl-3,5-diepipenicillinate 1,1-dioxide (13), and (3*S*,4*R*)-1-(1-methoxycarbonyl-2-methylprop-1-enyl)-2-oxo-3-phenylacetamidoazetidine-4-sulphinic acid (14): further treatment with DBN converts the derivatives (12) and (13) into the oxoazetidinesulphinic acid (14).

It is suggested that the epimerisations of penicillin sulphones at positions 6 and 3 occur by way of carbanionic species and that intermediates derived by β-elimination reactions do not intervene.

It is well established that penicillanates (1), can equilibrate under basic conditions with 6-epipenicillanates (2); such isomerisations are believed to occur by way of carbanionic intermediates (3). The epimerisations are often accompanied by the formation of thiazepinones (4), which are considered to arise from azetinone intermediates (5) formed from the carbanionic intermediates (3) by β-elimination reactions. It has been suggested that, under certain conditions, the foregoing reactions proceed by way of common intermediates, considered to be the azetinones (5) rather than the carbanionic species (3); objections, however, have been raised against this proposal.[3]

In principle, if azetinones (5) are involved in the epimerisations, there is the possibility of forming 5-epipenicillanates (6) and 5,6-diepipenicillanates (7). Whilst such derivatives have never been isolated from the epimerisations of penicillanates (1) and 6-epipenicillanates (2), this result may conceivably be ascribed to an unfavourable thermodynamic situation. Consequently, an examination of the behaviour of 5-epipenicillanates (6) and/or 5,6-diepipenicillanates (7), under conditions in which the derivatives (1) and (2) equilibrate, should define the epimerisation pathway. If azetinones (5) intervene, an equilibrium mixture of the penicillanates (1) and (2) will be produced; if not, interconversion of the derivatives (6) and (7) is the expected result.

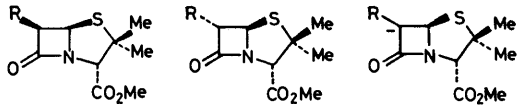
The availability of methyl benzylpenicillinate (1a),[4,5] methyl benzyl-6-epipenicillinate (2a),[6] and methyl benzyl-5-epipenicillinate (6a) [1,7] suggested that these compounds could be used to test the foregoing possibilities.

1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) has been shown to be a useful base for promoting the epimerisations of penicillanates with acidifying substituents, *e.g.* (1b), at position 6.[8] However, it is ineffective in the case of penicillinates, *e.g.* (1a), unless the derivatives are first converted into the trimethylsilyl ethers, *e.g.* (1c), by *NO*-bis(trimethylsilyl)acetamide (BSA).[6] Although their 6-hydrogen atoms may be expected to be more acidic than those of penicillinates, *e.g.* (1a), penicillinate 1-oxides, *e.g.* (8), usually require silylation with BSA prior to treatment with DBN in order to undergo epimerisations.[9] The acidity of the 6-hydrogen atoms is expected to be enhanced even further in the case of penicillinate 1,1-dioxides, *e.g.* (9); epimerisations of such derivatives, however, have not hitherto been described.

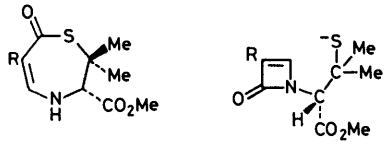
In a preliminary experiment, methyl benzylpenicillinate 1,1-dioxide (9) [10] was treated in deuteriochloroform with DBN. The reaction was monitored by n.m.r.

[1] Part 17, W. Baker, C. M. Pant, and R. J. Stoodley, *J.C.S. Perkin I*, 1978, 668.
[2] Preliminary communication, C. M. Pant and R. J. Stoodley, *J.C.S. Chem. Comm.*, 1977, 57.
[3] R. J. Stoodley, *Tetrahedron*, 1975, **31**, 2321.
[4] 'The Chemistry of Penicillin,' eds. H. T. Clarke, J. R. Johnson, and R. Robinson, Princeton University Press, Princeton, N.J., 1949, p. 93.
[5] M. R. Bell, J. A. Carlson, and R. Oesterlin, *J. Org. Chem.*, 1972, **37**, 2733.
[6] A. Vlietinck, E. Roets, P. Claes, G. Janssen, and H. Vanderhaeghe, *J.C.S. Perkin I*, 1973, 937.
[7] R. Busson and H. Vanderhaeghe, *J. Org. Chem.*, 1976, **41**, 2561.
[8] J. R. Jackson and R. J. Stoodley, *Chem. Comm.*, 1971, 647.
[9] P. Claes, A. Vlietinck, E. Roets, H. Vanderhaeghe, and S. Toppet, *J.C.S. Perkin I*, 1973, 932.
[10] Ref. 4, p. 177.

spectroscopy and a 1 : 2 mixture of the starting material and a new compound was rapidly produced. When the foregoing reaction was performed on a preparative scale



(1) (2) (3)



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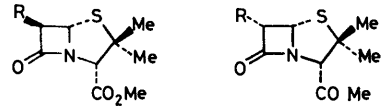
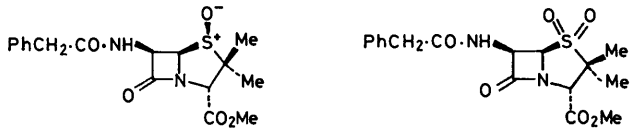
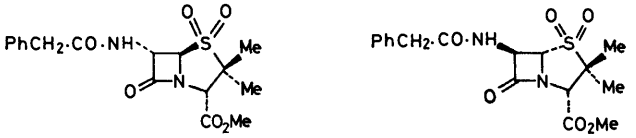


(6) (7)

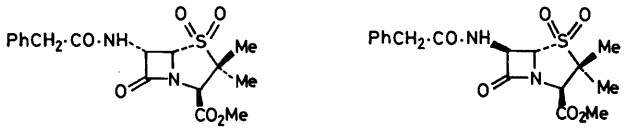
(a) R = $PhCH_2 \cdot CO \cdot NH$
(b) R = phthalimido
(c) R = $PhCH_2 \cdot C(OSiMe_3):N$



(8) (9)



(10) (11)



(12) (13)

and the product fractionated by silica-gel chromatography, the new compound was isolated in 37% yield. Elemental analysis indicated that it was isomeric with the starting sulphone (9) and spectroscopic evidence left little doubt that it was methyl benzyl-6-epipenicillinate 1,1-dioxide (10); in particular, n.m.r. spectroscopy showed the presence of *trans*-disposed [11] β-lactam protons [δ($CDCl_3$) 4.80 (d, *J* 1.5 Hz) and 5.15 (dd, *J* 1.5 and 8 Hz)]. Further evidence that the derivative was the 6-epimer (10) was indicated by performing the reaction in a 1 : 1 mixture of [$^2H_6$]dimethyl sulphoxide and deuterium oxide. The n.m.r. spectrum of the purified product was identical with that of the derivative (10) except that it lacked the signal at δ 5.15 and the signal at 4.80 appeared as a singlet; clearly, the material was the epimer (10) deuteriated at position 6. When re-subjected to the reaction conditions, the 6-epimer (10) equilibrated (2 : 1) with the starting sulphone (9).

Having established that the derivatives (9) and (10) were present as a 1 : 2 equilibrium mixture in the presence of DBN, the behaviour of methyl benzyl-5-epipenicillinate 1,1-dioxide (11) was examined. The reaction of the derivative (11), prepared in 77% yield by oxidation of methyl benzyl-5-epipenicillinate (6a) with potassium permanganate in aqueous acetic acid, with DBN was more complex. It was not possible to establish an equilibrium situation because of the rapidity of a competing reaction in which the base was consumed. However, by performing the reaction in deuteriochloroform and monitoring it by n.m.r. spectroscopy, it was possible to add sufficient base to deplete the starting material. Work-up at this stage yielded a neutral and an acidic fraction.

The neutral fraction contained two major components on t.l.c. and these were separated by silica-gel chromatography. The minor, less polar material, isolated in 17% yield, was shown to be an isomer of the starting sulphone (11) by elemental analysis. Its spectroscopic properties were very similar with those of methyl benzylpenicillinate 1,1-dioxide (9); however, its optical rotation {$[\alpha]_D$ −140° ($CHCl_3$)} was opposite in sign to that of the derivative (9) {$[\alpha]_D$ +172° ($CHCl_3$)}, establishing that it was methyl benzyl-3,5,6-triepipenicillinate 1,1-dioxide (12).* The major material, isolated in 43% yield, was also shown to be isomeric with the starting sulphone (11). Its spectroscopic properties compared well with those of methyl benzyl-6-epipenicillinate 1,1-dioxide (10); however, its optical rotation {$[\alpha]_D$ −164° ($CHCl_3$)} was similar in magnitude but opposite in sign to that of the derivative (10) {$[\alpha]_D$ +161° ($CHCl_3$)}, establishing that it was methyl benzyl-3,5-diepipenicillinate 1,1-dioxide (13).

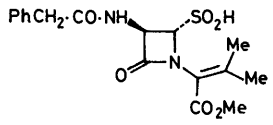
The acidic fraction, obtained in 23% yield, was identified as the oxoazetidinesulphinic acid (14), on the basis of its analytical and spectroscopic properties. N.m.r. spectroscopy was of particular value in establishing the structure since it revealed the presence of signals at δ 1.98 and 2.23 attributable to a geminal dimethyl group attached to a vinylic carbon atom, and at 4.68 (d, *J* 2 Hz) and 5.25 (dd, *J* 2 and 6 Hz), characteristic of *trans*-orientated β-lactam protons.

It is clear from the foregoing results that methyl benzyl-5-epipenicillinate 1,1-dioxide (11) does not

* In our preliminary communication,[2] this compound was incorrectly formulated as methyl benzyl-3,5-diepipenicillinate 1,1-dioxide; we apologise for this error.

[11] E. J. Corey and A. M. Felix, *J. Amer. Chem. Soc.*, 1965, **87**, 2518; I. McMillan and R. J. Stoodley, *Tetrahedron Letters*, 1966, 1205.

provide a suitable model for probing the nature of the intermediates involved in the epimerisation of methyl benzylpenicillinate 1,1-dioxide (9) at position 6. In the case of the derivative (11), the 3-proton is apparently more acidic than the 6-proton. Probably, epimerisation initially occurs at position 3 to give methyl benzyl-3,5-diepipenicillinate 1,1-dioxide (13) and this sulphone then interconverts with methyl benzyl-3,5,6-triepipenicillinate 1,1-dioxide (12). The isomerisation of the sulphone (11) to the derivative (13) must proceed by



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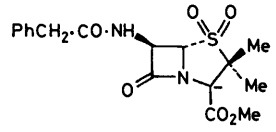

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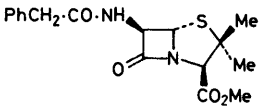

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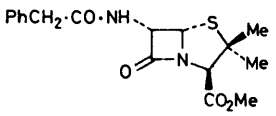

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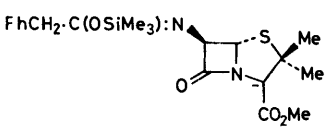

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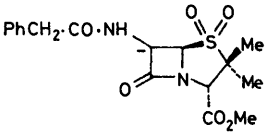

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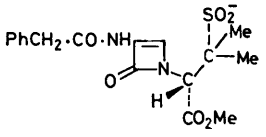

(20)

way of a carbanionic species, *i.e.* (15), since the sulphinic acid (14), the expected intermediate in the β-elimination pathway, was stable under the reaction conditions. In the epimerisation of the derivative (11) at position 3, the methoxycarbonyl group moves from a hindered *endo*-position to a less hindered *exo*-site; presumably, this relief in steric strain provides the driving force for the reaction.

The concomitant formation of the oxoazetidinesulphinic acid (14) from the reaction of methyl benzyl-5-epipenicillinate 1,1-dioxide (11) with DBN must involve a β-elimination reaction; this isomerisation is probably of the *E*1cb type,[12] proceeding by way of the carbanionic species (15). When the sulphone (11) was treated with an excess of DBN, the oxoazetidinesulphinic acid (14) was isolated in 80% yield. Clearly, the sulphones (12) and (13) must also undergo irreversible isomerisations to the oxoazetidinesulphinic acid (14). β-Elimination reactions of penicillanates, triggered by the base-induced removal of the hydrogen atoms at positions 3, are well documented.[3] The corresponding reactions of penicillanate 1-oxides, although much rarer, are also known,[3] whereas those of penicillanate 1,1-dioxides have not hitherto been described.

Vanderhaeghe and his co-workers have recently commented on the behaviour of methyl benzyl-5-epipenicillinate (6a) towards BSA and DBN.[7] In contrast with methyl benzylpenicillinate (1a) and methyl benzyl-6-epipenicillinate (2a), which formed a 1 : 3 equilibrium mixture in the presence of the reagents, methyl benzyl-5-epipenicillinate (6a) afforded methyl benzyl-3,5-diepipenicillinate (16) and methyl benzyl-3,5,6-triepipenicillinate (17) in the ratio of 4 : 1; there was no evidence for the formation of methyl benzyl-5,6-diepipenicillinate (7a). Clearly, the foregoing results and our results are complementary.

The Belgian workers proposed that the azetinone (5c) intervened in the interconversion of the derivatives (1a) and (2a); they also postulated that the isomerisation of methyl benzyl-5-epipenicillinate (6a) involved the carbanionic species (18). Whilst we agree with the latter postulate, we consider the former proposal to be unlikely. We suggest that the carbanionic species (3c) intervenes in the isomerisation of the penicillinates (1a) and (2a); similarly we consider that the carbanionic species (19) is involved in the isomerisation of the penicillinate 1,1-dioxides (9) and (10). In neither case do we believe that there is any isomerisation of the intermediates (3c) and (19) to the azetinones (5c) and (20).

EXPERIMENTAL

For general experimental details, see Part 1.[13] 60-MHz N.m.r. spectra were recorded with a Varian EM-360 spectrometer.

Methyl Benzylpenicillinate 1,1-*Dioxide* (9).—The sulphone (9), prepared by a literature method,[10] showed the following properties: m.p. 168—170 °C (lit.,[10] 173—174 °C), $\nu_{max.}$(KBr) 3 300 (N–H), 1 810 (β-lactam C=O), 1 755 (ester C=O), 1 665 (amide C=O), 1 535 (amide II), and 1 330 and 1 120 cm^{-1} (O=S=O), δ($CDCl_3$) 1.37 and 1.56 (each 3 H, s, *gem*-Me_2), 3.68 (2 H, s, $PhCH_2{\cdot}CO$), 3.84 (3 H, s, CO_2Me), 4.46 (1 H, s, $N{\cdot}CH{\cdot}CO_2Me$), 4.75 (1 H, d, *J* 4 Hz, $CH{\cdot}CH{\cdot}SO_2$), 6.12 (1 H, dd, *J* 4 and 9 Hz, $NH{\cdot}CH{\cdot}CH$), 6.9br (1 H, d, *J* 9 Hz, $CO{\cdot}NH{\cdot}CH$), and 7.35 (5 H, s, Ph) [addition of D_2O caused the signal at 6.9 to disappear and that at 6.12 to collapse to a d (*J* 4 Hz)]; *m/e* 316 ($M^+ - SO_2$) and 91 ($C_7H_7^+$, base peak).

Reaction of Methyl Benzylpenicillinate 1,1-*Dioxide* (9) *with DBN* (*with* D. F. Corbett).—(*a*) A solution of the sulphone (9) (0.500 g, 1.32 mmol) in chloroform (3 cm^3) was treated with DBN (0.078 g, 0.63 mmol) in chloroform (1.5 cm^3). After 12 h the mixture was diluted with chloroform and washed with M-hydrochloric acid followed by water. Evaporation of the dried ($MgSO_4$) organic layer and fractionation of the product by silica-gel chromatography (C_6H_6–Et_2O as eluant) afforded two components.

The first eluted material (0.121 g, 24%) was identical

[12] D. J. McLennan, *Quart. Rev.*, 1967, **21**, 490.
[13] I. McMillan and R. J. Stoodley, *J. Chem. Soc.* (*C*), 1968, 2533.

(t.l.c. and n.m.r. spectroscopy) with the starting sulphone (9).

The second eluted material (0.185 g, 37%) was *methyl benzyl-6-epipenicillinate* 1,1-*dioxide* (10), m.p. 124—125 °C (from C_6H_6–Et_2O), $[\alpha]_D$ +161° (1.0% in $CHCl_3$), $\nu_{max.}$ (film) 3 580 and 3 490 (N–H), 1 785 (β-lactam C=O), 1 750 (ester C=O), 1 665 (amide C=O), 1 525 (amide II), and 1 300 and 1 105 cm^{-1} (O=S=O), δ($CDCl_3$) 1.40 and 1.59 (each 3 H, s, *gem*-Me_2), 3.65 (2 H, s, $PhCH_2$·CO), 3.83 (3 H, s, CO_2Me), 4.42 (1 H, s, N·C*H*·CO_2Me), 4.80 (1 H, d, *J* 1.5 Hz, CH·C*H*·SO_2), 5.15 (1 H, dd, *J* 1.5 and 8 Hz, NH·C*H*·CH), 6.8br (1 H, d, *J* 8 Hz, CO·N*H*·CH), and 7.40 (5 H, s, Ph) [addition of D_2O caused the signal at 6.8 to disappear and that at 5.15 to collapse to a d (*J* 4.5 Hz)]; *m/e* 316 (M^+ – SO_2) and 91 ($C_7H_7^+$, base peak) (Found: C, 53.4; H, 5.1; N, 7.3. $C_{17}H_{20}N_2O_6S$ requires C, 53.7; H, 5.3; N, 7.4%).

(*b*) A solution of the sulphone (9) (0.250 g, 0.66 mmol) in a mixture of [$^2H_6$]dimethyl sulphoxide (1 cm^3) and deuterium oxide (1 cm^3) was treated with DBN (0.039 g, 0.031 mmol) for 1 h. Work-up and fractionation of the product as in (*a*) afforded methyl benzyl-[^{2}H]6-epipenicillinate 1,1-dioxide (0.092 g, 38%), δ($CDCl_3$) 1.42 and 1.60 (each 3 H, s, *gem*-Me_2), 3.64 (2 H, s, $PhCH_2$·CO), 3.86 (3 H, s, CO_2Me), 4.80 (1 H, s, CD·C*H*·SO_2), 6.7br (1 H, s, CO·N*H*·CD), and 7.36 (5 H, s, Ph) (addition of D_2O caused the signal at 6.7 to disappear).

Reaction of Methyl Benzyl-6-epipenicillinate 1,1-*Dioxide* (10) *with DBN* (*with* D. F. Corbett).—The sulphone (10) was treated with DBN in chloroform as described for the derivative (9). Work-up as before yielded a 3 : 1 mixture of the starting material and the derivative (9) (n.m.r. spectroscopy).

Methyl Benzyl-5-epipenicillinate 1,1-*Dioxide* (11).—A solution of methyl benzyl-5-epipenicillinate (6a) [1] (0.200 g, 0.56 mmol) in 80% aqueous acetic acid (3 cm^3) was treated over 0.5 h with a solution of potassium permanganate (0.193 g, 1.22 mmol) in water (1.5 cm^3). After a further 1 h, the mixture was treated with 30% aqueous hydrogen peroxide until the colour was discharged. The solution was then neutralised with sodium hydrogen carbonate solution and extracted with dichloromethane. Evaporation of the dried ($MgSO_4$) organic layer yielded the *sulphone* (11) (0.164 g, 75%), m.p. 128—130 °C (from $CHCl_3$–Et_2O), $[\alpha]_D$ –90° (1.0% in $CHCl_3$), $\nu_{max.}$(KBr) 3 300 (N–H), 1 810 (β-lactam C=O), 1 750 (ester C=O), 1 665 (amide C=O), 1 550 (amide II), and 1 325 and 1 135 cm^{-1} (O=S=O), $\lambda_{max.}$(EtOH) 206 nm (ε 9 300), δ($CDCl_3$) 1.33 and 1.60 (each 3 H, s, *gem*-Me_2), 3.60 (2 H, s, $PhCH_2$·CO), 3.78 (3 H, s, CO_2Me), 4.18 (1 H, s, N·C*H*·CO_2Me), 4.9—5.0 (2 H, m, NH·C*H*·C*H*·SO_2), 6.65br (1 H, d, *J* 7 Hz, CO·N*H*·CH), and 7.30 (5 H, s, Ph) (addition of D_2O caused the signals at 6.65 to disappear and that at 4.9—5.0 to collapse to a br s); *m/e* 316 (M^+ – SO_2) and 91 (base peak, $C_7H_7^+$) (Found: C, 53.9; H, 5.3; N, 7.2. $C_{17}H_{20}N_2O_6S$ requires C, 53.7; H, 5.3; N, 7.4%).

Reaction of Methyl Benzyl-5-epipenicillinate 1,1-*Dioxide* (11) *with DBN*.—(*a*) A solution of the sulphone (11) (0.150 g, 0.46 mmol) in deuteriochloroform (1 cm^3) was treated with DBN (0.028 g, 0.23 mmol). The reaction was monitored by n.m.r. spectroscopy and when the starting material had disappeared the mixture was diluted with chloroform and washed with dilute hydrochloric acid followed by water. The organic layer was extracted with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated to give a syrup (0.105 g) which contained two components on t.l.c. The components were separated by silica-gel chromatography [C_6H_6–Et_2O (9 : 1) as eluant].

The first eluted material (0.025 g, 17%) was *methyl benzyl-3,5,6-triepipenicillinate* 1,1-*dioxide* (12), m.p. 160 °C (from $CHCl_2$–Et_2O), $[\alpha]_D$ –140° (0.5% in $CHCl_3$), $\nu_{max.}$(KBr) 3 280 (N–H), 1 795 (β-lactam C=O), 1 745 (ester C=O), 1 660 (amide C=O), 1 530 (amide II), and 1 320 and 1 120 cm^{-1} (O=S=O); $\lambda_{max.}$(EtOH) 211 nm (ε 15 200), δ($CDCl_3$) 1.35 and 1.55 (each 3 H, s, *gem*-Me_2), 3.65 (2 H, s, $PhCH_2$·CO), 3.80 (3 H, s, CO_2Me), 4.46 (1 H, s, N·C*H*·CO_2Me), 4.75 (1 H, d, *J* 4.2 Hz, CH·C*H*·SO_2), 6.11 (1 H, dd, *J* 4.2 and 10 Hz, NH·C*H*·CH), 6.9br (1 H, d, *J* 10 Hz, CO·N*H*·CH), and 7.32 (5 H, s, Ph) [addition of D_2O caused the signal at 6.9 to disappear and that at 6.11 to collapse to a d (*J* 4.2 Hz)]; *m/e* 316 (M^+ – SO_2) and 91 (base peak, $C_7H_7^+$) (Found: C, 53.6; H, 5.5; N, 7.0. $C_{17}H_{20}N_2O_6S$ requires C, 53.6; H, 5.3; N, 7.3%).

The second eluted material (0.064 g, 43%) was *methyl benzyl-3,5-diepipenicillinate* 1,1-*dioxide* (13), m.p. 126—127 °C (from $CHCl_3$–Et_2O), $[\alpha]_D$ –164° (1.14% in $CHCl_3$), $\nu_{max.}$(KBr) 3 600 and 3 520 (N–H), 1 790 (β-lactam C=O), 1 755 (ester C=O), 1 665 (amide C=O), 1 530 (amide II), and 1 310 and 1 115 cm^{-1} (O=S=O), $\lambda_{max.}$ 207 nm (ε 10 700), δ($CDCl_3$) 1.35 and 1.55 (each 3 H, s, *gem*-Me_2), 3.60 (2 H, s, $PhCH_2$·CO), 3.78 (3 H, s, CO_2Me), 4.37 (1 H, s, N·C*H*·CO_2Me), 4.80 (1 H, d, *J* 1.5 Hz, CH·C*H*·SO_2), 5.07 (1 H, dd, *J* 1.5 and 8 Hz, NH·C*H*·CH), 6.7br (1 H, d, *J* 8 Hz, CO·N*H*·CH), and 7.3 (3 H, s, Ph) [addition of D_2O caused the signal at 6.7 to disappear and that at 5.07 to collapse to a d (*J* 1.5 Hz)]; *m/e* 316 (M^+ – SO_2) and 91 (base peak, $C_7H_7^+$) (Found: C, 53.7; H, 5.3; N, 8.4. $C_{17}H_{20}N_2O_6S$ requires C, 53.7; H, 5.3; N, 7.4%).

The sodium hydrogen carbonate washing was acidified with dilute hydrochloric acid and extracted with chloroform. Evaporation of the dried ($MgSO_4$) organic layer gave (3S,4R)-1-(1-*methoxycarbonyl*-2-*methylprop*-1-*enyl*)-2-*oxo*-3-*phenylacetamidoazetidine*-4-*sulphinic acid* (14) (0.04 g, 23%), m.p. 130 °C (from $CHCl_3$), $[\alpha]_D$ +160° (0.9% in $CHCl_3$), $\nu_{max.}$ (film) 3 300br (N–H), 2 480br (OH), 1 780 (β-lactam C=O), 1 725 (ester C=O), and 1 635 cm^{-1} (amide C=O); $\lambda_{max.}$(EtOH) 208 (ε 14 000) and 225sh nm (7 000), δ($CDCl_3$) 1.98 and 2.23 (each 3 H, s, *gem*-Me_2), 3.66 (2 H, s, $PhCH_2$·CO), 3.83 (3 H, s, CO_2Me), 4.68 (1 H, d, *J* 2 Hz, CH·C*H*·SO_2H), 5.25 (1 H, dd, *J* 2 and 6 Hz, NH·C*H*·CH), 7.30 (5 H, s, Ph), 7.60br (1 H, s, SO_2H), and 7.9br (1 H, d, *J* 6 Hz, NH) [addition of D_2O caused the signals at 7.6 and 7.9 to disappear and that at 5.25 to collapse to a d (*J* 2 Hz)]; *m/e* 314 (M^+ – SO_2H) and 91 (base peak, $C_7H_7^+$) (Found: C, 53.7; H, 5.3; N, 7.4. $C_{17}H_{20}N_2O_6S$ requires C, 53.7; H, 5.3; N, 7.4%).

(*b*) A solution of the sulphone (11) (0.050 g, 0.15 mmol) in deuteriochloroform (0.5 cm^3) was treated dropwise with a 20% solution of DBN in deuteriochloroform until formation of the sulphinic acid (14) appeared to be complete (n.m.r. spectroscopy). Work-up as in (*a*) afforded the sulphinic acid (14) (0.040 g, 80%).

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