Reactions of 2,2,2-Trichloroethyl 6-Diazopenicillanate with Aromatic Aldehydes. *X*-Ray Crystal Structures of (3*S*,8a*S*)-2,2,2-Trichloroethyl 2,3-Dihydro-6-(4-methoxyphenyl)-2,2-dimethyl-5-oxo-5*H*,8a*H*-thiazolo[2,3-*b*][1,3]oxazine-3-carboxylate and (2*S*,5*S*)-2,2,2-Trichloroethyl-4-formyl-2-(4-methoxyphenyl)-6,6-dimethyl-3-oxotetrahydro-1,4-thiazine-5-carboxylate.

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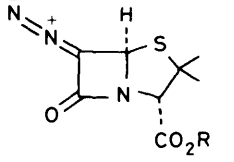
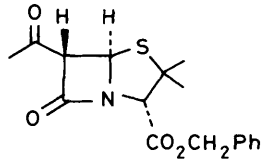
Treatment of 6-diazopenicillanate (**1**) with aromatic aldehydes in the presence of Lewis acids provides spiro epoxides, oxazinones, and thiazepines, the product distribution depending upon the particular aldehyde and Lewis acid catalyst used. The structure of the oxazinone (**5**) derived from 4-methoxybenzaldehyde, was established by an *X*-ray crystal structure determination. An explanation for the formation of these products is proposed, and 6-acylpenicillanate intermediates either isolated or trapped. The epoxidation of the oxazinone (**5**) by *m*-chloroperoxybenzoic acid provided the tetrahydrothiazine (**29**), identified by *X*-ray crystallography.

6-Diazopenicillanates have been used to prepare a range of penicillanates with a wide variety of C-6 substituents.[1] In many of the newer β-lactams, of interest either as antibacterials or β-lactamase inhibitors, the acylamino side-chain of the penicillins is omitted, and replaced by either hydrogen or a simple or substituted alkyl group. We here describe reactions between 2,2,2-trichloroethyl 6-diazopenicillanate (**1**), a crystalline,



(1) R = CH_2CCl_3
(2) R = CH_2Ph

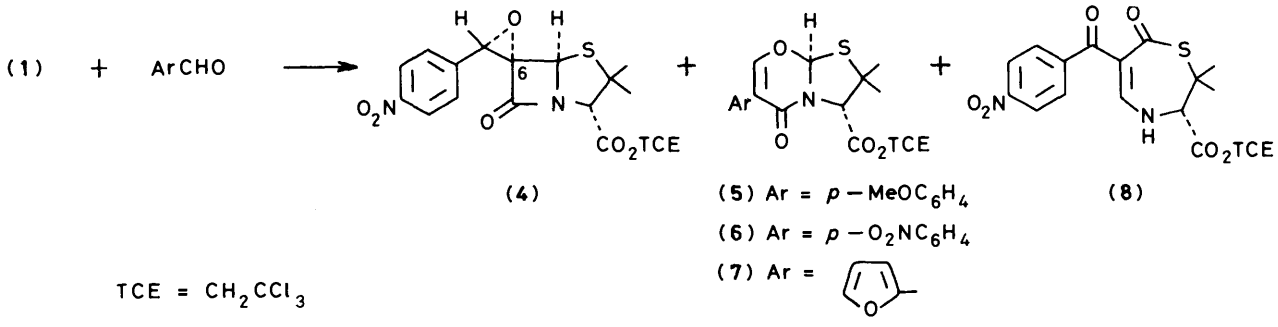


(3)

readily available diazo compound, and a series of aromatic aldehydes, together with aspects of the chemistry of the products.[2] During the course of our work Karady *et al.*[3] published results on the zinc chloride-catalysed reactions between 6-diazopenicillanate (**2**) and acetaldehyde, the 6α-acetylpenicillanate (**3**) being formed efficiently, and Sheehan had reported his results on the boron trifluoride–diethyl ether-catalysed reactions between 6-diazopenicillanate (**1**) and aromatic aldehydes and imines.[4,5]

Results and Discussion

Lewis Acid-catalysed Reactions with Aromatic Aldehydes.— Addition of a catalytic quantity of boron trifluoride–diethyl ether to a solution of the diazopenicillanate (**1**)[6] and an aromatic aldehyde in dichloromethane at 0—5 °C caused nitrogen evolution. From the reaction with 4-methoxybenzaldehyde, the oxazinone (**5**) (41%) was isolated after chromatography, in contrast 4-nitrobenzaldehyde gave the spiro-epoxide (**4**) (17%), and the oxazinone (**6**) (13%), and furfuraldehyde provided the oxazinone (**7**) (36%). In our hands little reaction was observed between the diazopenicillanate (**1**) and 4-nitrobenzaldehyde in the presence of a catalytic quantity of anhydrous zinc chloride, but tin(IV) chloride promoted rapid evolution of nitrogen in this system and led to the isolation, after column chromatography, of the spiro epoxide (**4**) (8%), the oxazinone (**6**) (15%), and the thiazepine (**8**) (38%).



(1) + ArCHO → (4) + (5) Ar = *p*-$MeOC_6H_4$ + (8)
(6) Ar = *p*-$O_2NC_6H_4$
(7) Ar =
TCE = CH_2CCl_3

These products were all separated and characterized spectro-

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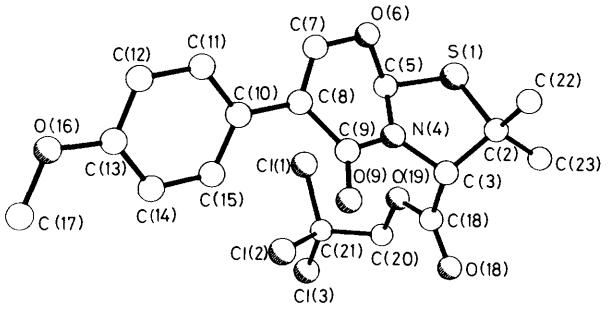
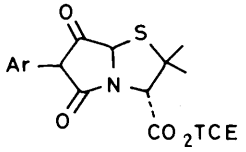


Figure 1. Molecular structure of (**5**) showing the crystallographic numbering scheme used

scopically. The epoxide (**4**) is known, and our spectroscopic data were identical with those reported.[5] The configuration at C-6 was not confirmed, but that shown is consistent with the mechanism outlined below. The configuration of the other epoxide chiral centre follows from the observation of an n.O.e. enhancement for 5-H on irradiation of the epoxide proton.

The structure of the oxazinone (**5**) from the 4-methoxybenzaldehyde reaction was established by *X*-ray diffraction. Figure 1 shows a projection of the molecule in the solid state



(**9**)

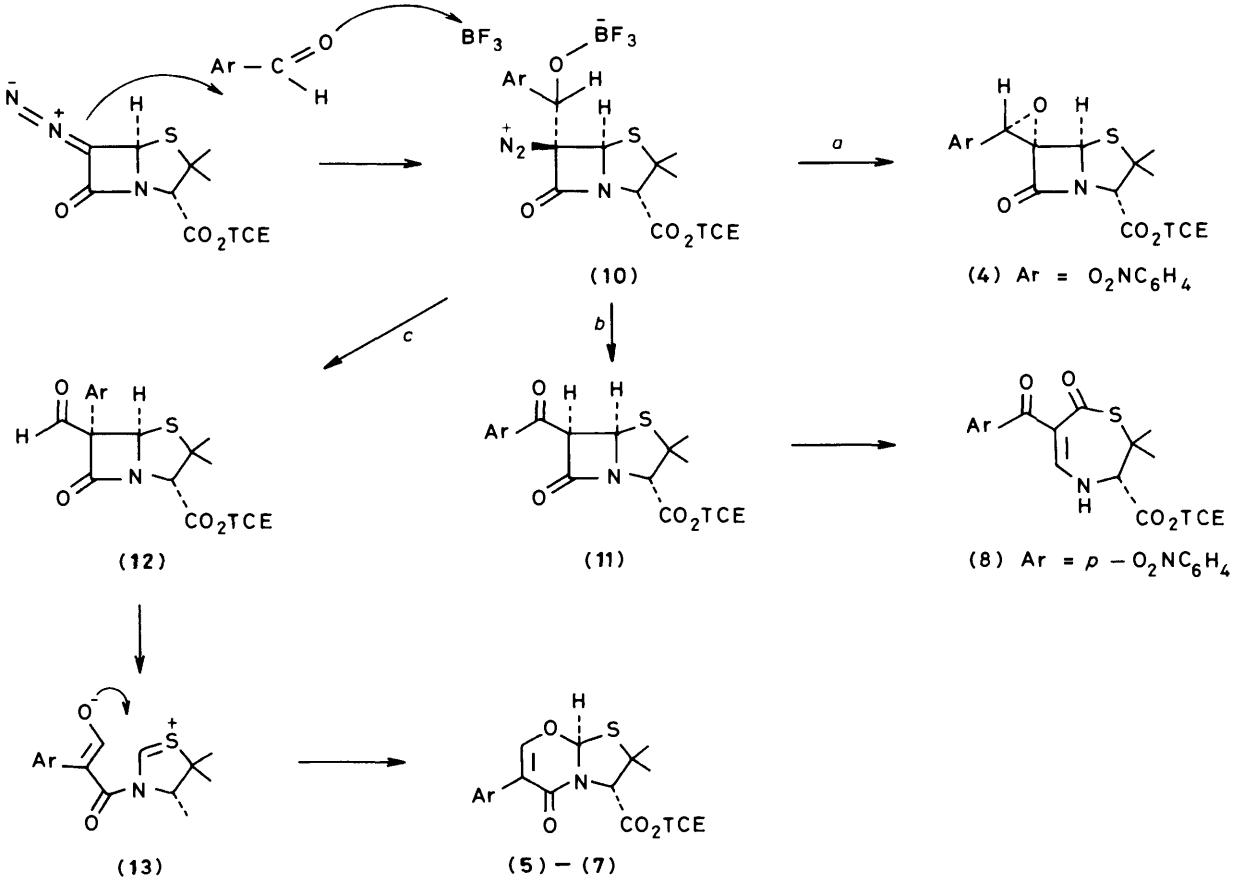
which clearly establishes the structure as that shown in formula (**5**). This product would appear to be identical with that reported by Sheehan, to which structure (**9**: Ar = *p*-$MeOC_6H_4$) was assigned.[5] The other oxazinones (**6**) and (**7**) were identified by spectroscopic comparison with (**5**), the oxazinone (**6**) being identified as (**9**; Ar = *p*-$NO_2C_6H_4$) by Sheehan.[5]

The thiazepine (**8**), the major product from the tin(IV) chloride–4-nitrobenzaldehyde reaction, was identified from its spectroscopic data by comparison with other known penicillanate-derived thiazepines.[7]

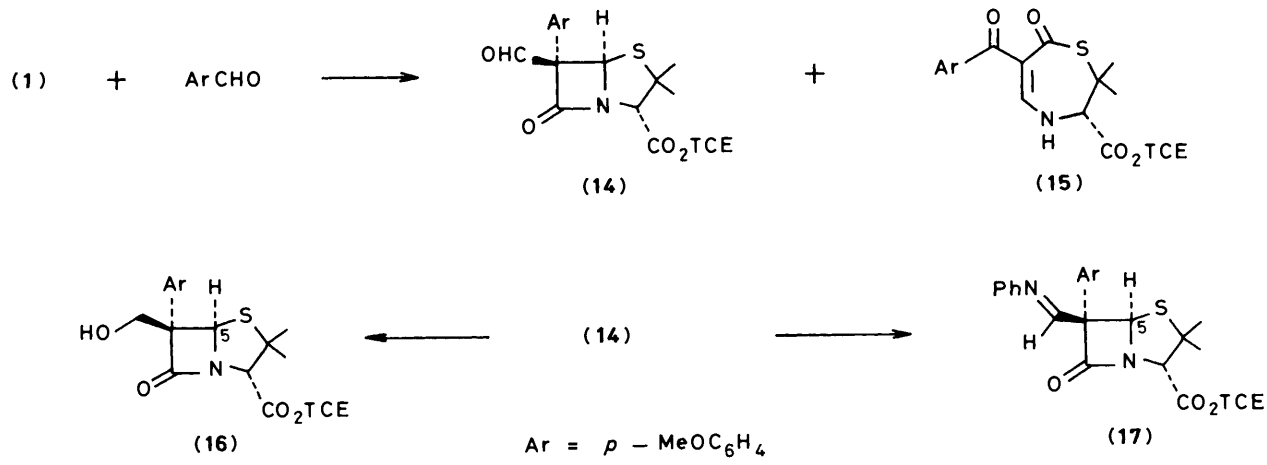
The formation of these products can be explained in terms of the reaction pathways outlined in Scheme 1.[8] Electrophilic attack of the aromatic aldehyde onto the less hindered α-face of the 6-diazopenicillanate provides the zwitterionic intermediate (**10**) which can rearrange in three ways. Cyclization with inversion of configuration at C-6, path (a), would give the (6*S*)-spiro epoxide (**4**). Alternatively, migration of hydride provides the unstable 6β-acylpenicillanate (**11**), which would be expected to rearrange to the thiazepine (**8**) on chromatography [path (b)].[4,9] Alternatively, it may be that the 6-acylpenicillanate (**11**) rearranges to the thiazepine in the presence of Lewis acid before work-up.[10] Migration of the aryl group *via* path (c) gives the 6β-formylpenicillanate (**12**) which could provide the oxazinones (**5**)—(**7**) *via* ring-opening and closing.[11]

This scheme is consistent with the observed product distributions. For the electron-rich aromatic aldehydes, the aryl migration step is faster than cyclization to an epoxide. Only in the case of 4-nitrobenzaldehyde was epoxide formation observed.

It was found that cooling the crude reaction mixture obtained from the 6-diazopenicillanate–4-methoxybenzaldehyde reaction before chromatography gave a crystalline product which was



Scheme 1

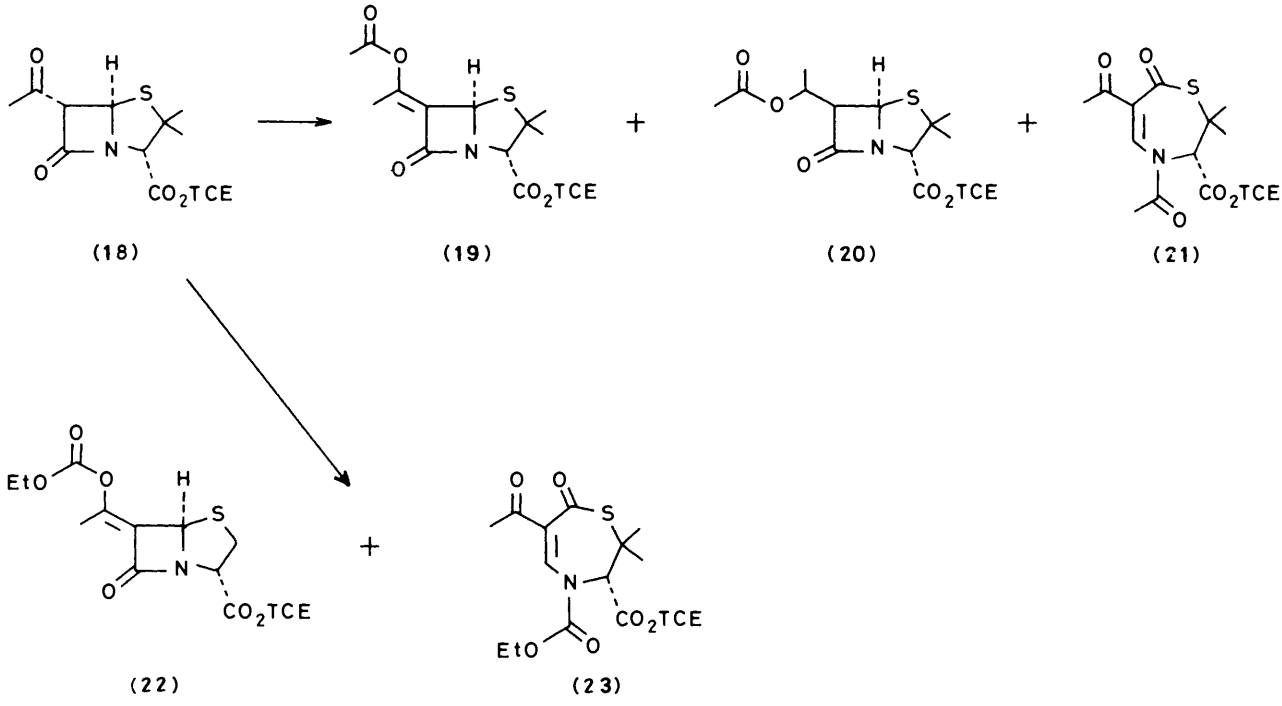


isolated in 30% yield and which was identified as aldehyde (**14**). The thiazepine (**15**) was also obtained from the mother liquor from this reaction (7%). The aldehyde (**14**) was rather unstable, and rearranged in solution to provide the oxazinone (**5**), $t_{\frac{1}{2}}$(20 °C) *ca.* 2 h. Reduction of the aldehyde (**14**) with sodium borohydride gave the alcohol (**16**) (53%) together with rearranged oxazinone (**5**) (20%), and treatment with aniline provided the imine (**17**) (50%). Unfortunately, neither the alcohol (**16**) nor the imine (**17**) gave crystals suitable for *X*-ray analysis which would have confirmed the configuration assigned to C-6. However on irradiation of 5-H for both the alcohol (**16**) and the imine (**17**), an n.O.e. enhancement of the ortho-aromatic protons was observed, which is consistent with the C-6 stereochemistry shown.

Enolate Chemistry of 6-Acylpenicillanates.—6β-Oxo-, 6β-acyl-, or 6β-(8-oxoalkyl)-penicillanates (**11**) were not isolated from our reactions, however such intermediates are known to be unstable, rearranging to thiazepines on silica gel chromatography.[9] It was decided to study aspects of the enolate chemistry of a preformed 6-acylpenicillanate to see whether new substituents could be introduced at C-6 prior to thiazepine formation.[12] It should then be possible to demonstrate the presence of 6-oxopenicillanates (**11**) in the product mixture from our tin(IV) chloride–catalysed 6-diazopenicillanate–4-nitrobenzaldehyde reaction.

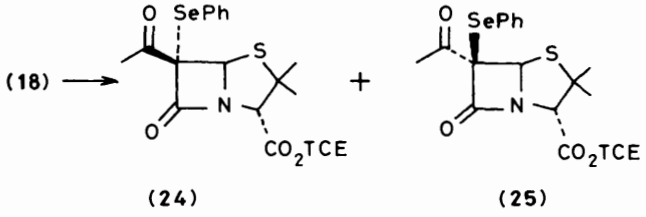
According to the published procedure, the 6-diazopenicillanate (**1**) was treated with acetaldehyde in the presence of a trace of anhydrous zinc chloride to prepare the 6α-acetylpenicillanate (**18**) (70%) which was isolated but not purified. This oxopenicillanate was then stirred in dichloromethane with equimolar equivalents of acetyl chloride and triethylamine. Three products were isolated and separated by chromatography. They were identified as the two enol esters (**19**) (35%) and (**20**) (4%), differentiated by the observation of an n.O.e. enhancement of 5-H on irradiation of the exocyclic methyl group for the minor but not for the major isomer, and the *N*-acetylated thiazepine (**21**) (18%).

Similar treatment of the 6-acetylpenicillanate (**18**) with ethyl chloroformate and triethylamine provided the enol carbonate (**22**) (11%) together with the *N*-ethoxycarbonylthiazepine (**23**) (22%). However attempts to functionalize the 6-acetylpenicillanate (**18**) on carbon at C-6 using base-catalysed



reactions with other electrophiles were generally unsuccessful. Treatment with methyl iodide, epichlorohydrin, or methyl methanethiosulphonate, in the presence of base, simply give rise to the rearranged thiazepine. Only benzeneselenenyl chloride gave rise to functionalization at C-6, a 5:1 mixture of products being obtained which were tentatively identified as the 6-phenylseleno derivatives (**24**) and (**25**), and from which the major isomer (**24**) was isolated by crystallization. The C-6 configuration shown in formula (**24**) for the major isomer was not confirmed, but is consistent with approach of the benzeneselenenyl electrophile to the less hindered face of C-6.

The tin(IV) chloride-catalysed reaction between 6-diazopenicillanate (**1**) and 4-nitrobenzaldehyde was then repeated, except that the crude reaction mixture was treated with an excess of acetyl chloride and triethylamine before chromatography. In this case five products were isolated and identified as the spiro epoxide (**4**) and the oxazinone (**6**) isolated previously, together with the two enol esters (**26**) (14%) and (**27**) (2%) and the *N*-acetylthiazepine (**28**) (8%). The isolation of these enol ester products is consistent with the presence of the 6-oxopenicillanate (**11**; Ar = *p*-$NO_2C_6H_4$) in the crude reaction mixture from the 6-diazopenicillanate–4-nitrobenzaldehyde reaction. In our hands at least, this oxopenicillanate would appear to be unstable to chromatography.[5]



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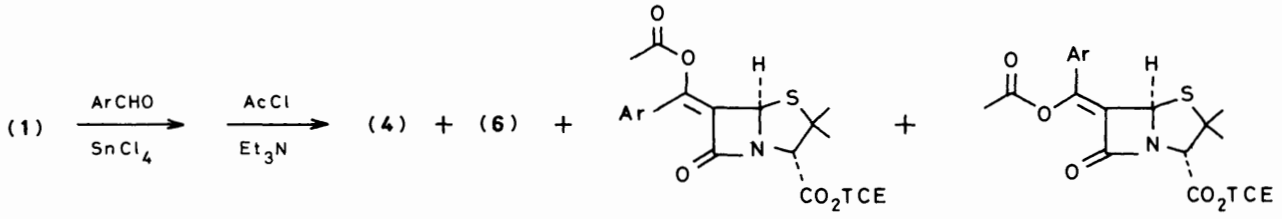

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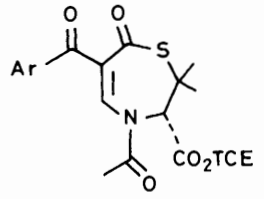
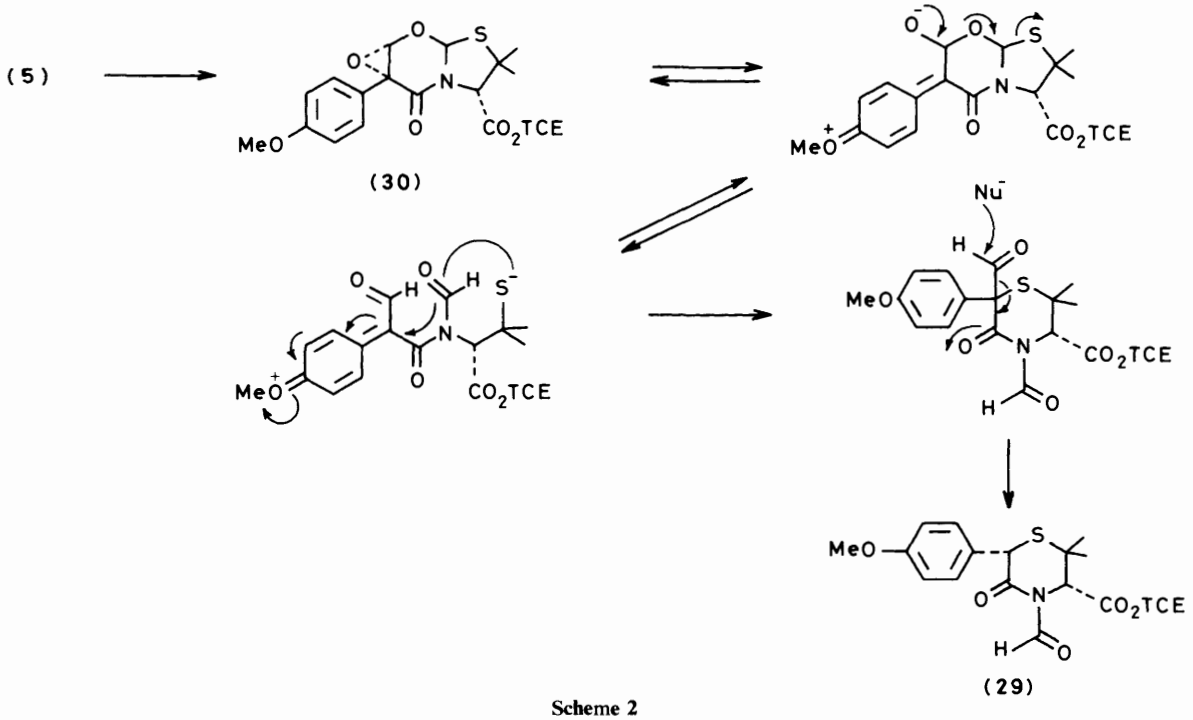


(28)

Ar = $p-O_2NC_6H_4$



(30) (29)

Scheme 2

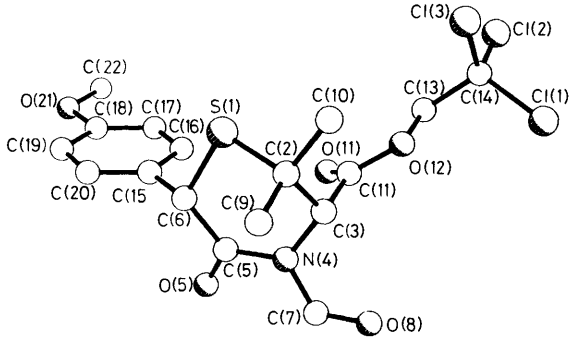
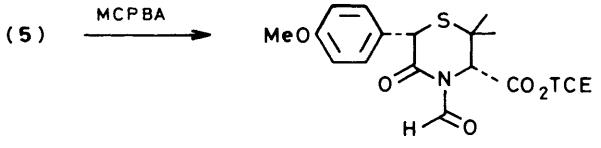


Figure 2. Molecular structure of (**29**) showing the crystallographic numbering scheme used

Oxidation of the Thiazolo-oxazinone (**5**).—Oxidation of the oxazinone (**5**) was briefly studied to see whether sulphoxides analogous to penicillanate sulphoxides could be prepared and rearranged. It was found that treatment of the 4-methoxyphenyloxazinone (**5**) with *m*-chloroperoxybenzoic acid gave a complex mixture of products from which a major product crystallized out from the chromatographed mixture (36% yield). This product could not be identified on the basis of its spectroscopic data, and so was examined by *X*-ray diffraction. This *X*-ray study established the structure of the crystalline product as the tetrahydro-1,4-thiazine (**29**); Figure 2 shows



(**29**)

a projection of the molecule which clearly defines its stereochemistry.

The mechanism of formation of this rearranged reduced thiazine was not investigated, but one possibility is outlined in Scheme 2. It may be that the epoxide (**30**) is formed initially, but that this is unstable to the fragmentation–cyclization process shown. Oxidation of the other oxazinones was not investigated.

Experimental

I.r. spectra were measured on a Perkin-Elmer 297 spectrophotometer, and ^{1}H n.m.r. spectra on a Bruker WM 250 spectrometer (250 MHz). Mass spectra were recorded on Varian VG 70-70F, AEI MS 30, and Varian VG 2AB spectrometers. M.p.'s were determined on a Kofler hot-stage apparatus and are uncorrected. Column chromatography refers to short-path chromatography using either Hopkins and Williams MFC t.l.c. grade or Merck Kieselgel 60H silica gel. All solvents were dried and distilled before use. Ether refers to diethyl ether throughout; light petroleum to the fraction b.p. 60—80° C.

Reactions between 6-Diazopenicillanate (**1**) *and Aromatic Aldehydes.—With 4-methoxybenzaldehyde.* Boron trifluoride–diethyl ether (2 drops) was added to a solution of the 6-diazopenicillanate (**1**) (2g, 5.6 mmol) and 4-methoxybenzaldehyde (0.91 g, 6.6 mmol) in dichloromethane (100 ml) at −5 °C. After 30 min the reaction mixture was washed with aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated under reduced pressure, and the residue chromatographed using ethyl acetate–light petroleum (1:9) as eluant. The first product off the column was identified as (3S,8aS)-2,2,2-*trichloroethyl* 2,3-*dihydro*-6-(4-*methoxyphenyl*)-2,2-*dimethyl*-5-*oxo*-5H,8aH-*thiazolo*[2,3-b][1,3]*oxazine*-3-*carboxylate* (**5**) (1.1 g, 41%), m.p. 141—142 °C (lit.,[5] m.p. 135—136 °C) (Found: M^+, 464.9970. $C_{18}H_{18}{}^{35}Cl_3NO_5S$ requires M, 464.9971); $\nu_{max.}$($CHCl_3$) 1 760, 1 660, 1 600, 1 510, and 1 390 cm^{-1}; δ_H($CDCl_3$) 1.58 and 1.85 (each 3 H, s, Me), 3.82 (3 H, s, OMe), 4.81 (2 H, s, CH_2CCl_3), 4.99 (1 H, s, 3-H), 6.84 (1 H, s, 8a-H), 6.90 and 7.42 (each 2 H, d, *J* 9 Hz, ArH), and 7.29 (1 H, s, 7-H); δ_C($CDCl_3$) 24.25 and 34.02 (each q, Me), 53.33 (s, 2-C), 55.30 (q, OMe), 70.26 (d, 3-C), 75.0 (t, CH_2CCl_3), 94.22 (s, CCl_3), 95.34 (d, 8a-C), 113.95 (d, ArC), 117.03 (s, 6-C), 124.00 (s, ArC), 129.63 (d, Ar C), 152.81 (d, 7-C), 159.54 (s, ArC), 161.04 (s, 5-C), and 167.2 (s, CO_2); *m/z* 465 (M^+).

When this reaction was repeated using 6-diazopenicillanate (**1**) (0.5 g, 1.39 mmol) and 4-methoxybenzaldehyde (0.23 g, 1.67 mmol) and the crude reaction product dissolved in ethyl acetate, crystallization was observed with time at −3 °C. Light petroleum was then added to the reaction mixture and the crystals filtered off to provide 2,2,2-*trichloroethyl* 6β-*formyl*-6α-(4-*methoxyphenyl*)*penicillanate* (**14**) (190 mg, 30%), m.p. 106—107 °C; $\nu_{max.}$($CHCl_3$) 1 780, 1 765, and 1 720 cm^{-1}; δ_H($CDCl_3$) 1.59 and 1.68 (each 3 H, s, Me), 3.82 (3 H, s, OMe), 4.64 (1 H, s, 3-H), 4.76 and 4.78 (each 1 H, d, *J* 12 Hz, each $HCHCCl_3$), 5.61 (1 H, s, 5-H), 6.94—7.38 (4 H, m, ArH), and 9.53 (1 H, s, CHO). The mother liquor was then run on a preparative t.l.c. plate using ethyl acetate–ether (3:2) as eluant to provide (3S)-2,2,2-*trichloroethyl* 2,3,4,7-*tetrahydro*-6-(4-*methoxybenzoyl*)-2,2-*dimethyl*-7-*oxo*-1,4-*thiazepine*-3-*carboxylate* (**15**) (45 mg, 7%), as a pale yellow oil; $\nu_{max.}$($CHCl_3$) 3 275, 1 760, and 1 650 cm^{-1}; δ_H($CDCl_3$) 1.65 and 1.75 (each 3 H, s, Me), 3.81 (3 H, s, OMe), 4.46 (1 H, d, *J* 6 Hz, 3-H), 4.75 and 4.83 (each 1 H, d, *J* 13 Hz, $HCHCCl_3$), 6.85 (2 H, m, ArH), 7.42 (1 H, d, *J* 8 Hz, 5-H), 7.5 (1 H, m, NH), and 7.65 (2 H, m, ArH); δ_C($CDCl_3$) 27.36 and 28.71 (each q, Me), 45.88 (s, 2-C), 55.47 (q, OMe), 68.64 (d, 3-C), 75.48 (t, CH_2CCl_3), 94.19 (s, CCl_3), 113.67, and 131.54 (d, ArC) 115.70 (s, 6-C), 132.06 and 162.97 (s, ArC), 149.30 (d, 5-C), 166.72 190:90, and 194.27 (s, C=O).

With 4-nitrobenzaldehyde. Boron trifluoride–diethyl ether (2 drops) was added to a solution of the diazopenicillanate (**1**) (0.5 g, 1.39 mmol) and 4-nitrobenzaldehyde (0.21 g, 1.39 mmol) in dichloromethane (20 ml) at 0 to 5 °C. After 30 min the reddish solution was concentrated under reduced pressure, and chromatographed on silica using ethyl acetate–light petroleum, gradient elution, as eluant. The first eluted product was identified as (2S,6′S)-2,2,2-*trichloroethyl* 2-(4-*nitrophenyl*)-*spiro*[*oxirane*-1,6′-*penicillanate*] (**4**) (17%), m.p. 124—125 °C (lit.,[5] m.p. 137—138 °C) (Found: M^+, 479.9721. $C_{17}H_{15}{}^{35}Cl_3N_2O_6S$ requires M^+, 479.9716); $\nu_{max.}$($CHCl_3$) 1 785, 1 760, 1 520, and 1 345 cm^{-1}; δ_H($CDCl_3$) 1.42 and 1.57 (each 3 H, s, Me), 4.44 (1 H, s, epoxide H), 4.63 (1 H, s, 3-H), 4.80 (2 H, s, CH_2CCl_3), 5.68 (1 H, s, 5-H), and 7.69 and 8.27 (each 2 H, m, ArH); *m/z* 480 (M^+); δ_C($CDCl_3$) 25.17 and 34.08 (q, Me), 61.92 (d, epoxide C), 63.46 (s, 2-C), 69.91 and 70.40 (d, 3-C and 5-C), 74.98 (t, CH_2CCl_3), 77.42 (s, 6-C), 93.92 (s, CCl_3), 123.69 and 127.56 (d, ArC), 138.98 and 148.51 (s, ArC), and 165.7 and 170.10 (s, C=O). The second eluted product was identified as (3S,8aS)-2,2,2-*trichloroethyl* 2,3-*dihydro*-2,2-*dimethyl*-6-(4-*nitrophenyl*)-5-*oxo*-5H,8aH-*thiazolo*[2,3-b][1,3]*oxazine*-3-*carboxylate* (**6**) (85 mg, 13%), m.p. 157—160 °C from CH_2Cl_2–light petroleum (lit.,[5] amorphous powder) (Found: M^+, 479.9714. $C_{17}H_{15}{}^{35}Cl_3N_2O_6S$ requires M, 479.9716); $\nu_{max.}$(Nujol) 1 750, 1 660, 1 580, and 1 510 cm^{-1}; δ_H($CDCl_3$) 1.60 and 1.85 (each 3 H, s, Me), 4.82 and 4.84 (each 1 H, d, *J* 12 Hz, $HCHCCl_3$), 5.00 (1 H, s, 3-H), 6.89 (1 H, s, 8aH), 7.50 (1 H, s, 7-H), and 7.73 and 8.23 (each 2 H, m, ArH); δ_C($CDCl_3$) 24.19 and 33.93 (each q, Me), 53.45 (s, 2-C), 70.33 (d, 3-C), 75.07 (t, CH_2CCl_3), 94.11 (s, CCl_3), 95.91 (d, 8a-C), 115.52 (s, 6-C), 123.65 and 128.81 (each d, ArC), 138.46 and 147.50 (each s, ArC), 155.46 (d, 7-C), 159.94 (s, 5-C), and 166.88 (s, CO_2); *m/z* 480 (M^+).

Tin(IV) chloride (1 drop) was added to a solution of the 6-diazopenicillanate (**1**) (125 mg, 0.35 mmol) and 4-nitrobenzal-

dehyde (53 mg, 0.35 mmol) in dichloromethane (5 ml) at room temperature. Rapid evolution of nitrogen was observed, and after 5 min the mixture was concentrated under reduced pressure to leave a foam which was chromatographed on silica using gradient elution with ethyl acetate–hexane as eluant. The spiro-epoxide (**4**) and the oxazinone (**6**) were eluted first followed by (3S)-2,2,2-*trichloroethyl* 2,3,4,7-*tetrahydro*-2,2-*dimethyl*-6-(4-*nitrobenzoyl*)-7-*oxo*-1,4-*thiazepine*-3-*carboxylate* (**8**) (64 mg, 38%), m.p. 104—106 °C (from chloroform) (Found: $M^+ - CO_2CH_2CCl_3 - CO$, 277.0634. $C_{13}H_{13}N_2O_3S$ requires *M*, 277.0647); $\nu_{max.}$(Nujol) 3 240, 1 750, and 1 650 cm^{-1}; δ_H[$(CD_3)_2SO$] 1.65 and 1.79 (each 3 H, s, Me), 4.86 (1 H, br s, 3-H), 4.95 and 5.05 (each 1 H, d, *J* 12 Hz, $HCHCCl_3$), 7.65 and 8.23 (each 2 H, m, ArH), 7.78 (1 H, br s, 5-H), and 9.46 (1 H, m, NH); δ_C($CDCl_3$) 26.96 and 28.53 (each q, Me), 46.18 (s, 2-C), 68.76 (d, 3-C), 75.57 (t, CH_2CCl_3), 93.74 (s, CCl_3), 115.42 (s, 6-C), 123.44 and 128.93 (each d, ArC), 145.73 and 149.06 (each s, ArC), 150.18 (d, 5-C), and 166.34, 190.42, and 193.25 (each s, C=O).

With furfuraldehyde. Following the procedure outlined above, 6-diazopenicillanate (**1**) (0.5 g) and furfuraldehyde (0.12 ml, 1.39 mmol, freshly distilled) gave, after repeated chromatography on silica gel using ethyl acetate–light petroleum, 1:9, as eluant, (3S,8aS)-2,2,2-*trichloroethyl* 6-(2-*furyl*)-2,3-*dihydro*-2,2-*dimethyl*-5-*oxo*-5H,8aH-*thiazolo*[2,3-b][1,3]*oxazine*-3-*carboxylate* (**7**) (215 mg, 36%), an unstable, pale yellow, oil (Found: M^+, 424.9641. $C_{15}H_{14}{}^{35}Cl_3NO_5S$ requires *M*, 424.9654); $\nu_{max.}$($CHCl_3$) 1 760, 1 680, and 1 420 cm^{-1}; δ_H($CDCl_3$) 1.58 and 1.81 (each 3 H, s, Me), 4.82 and 4.83 (each 1 H, d, *J* 13 Hz, $HCHCCl_3$), 4.97 (1 H, s, 3-H), 6.43 (1 H, dd, *J* 1.5, 3 Hz, furyl H), 6.78 (1 H, s, 8a-H), 6.87 (1 H, d, *J* 3 Hz, furyl H), 7.33 (1 H, d, *J* 1.5 Hz, furyl H), and 7.68 (1 H, s, 7-H); *m/z* 425 (M^+).

2,2,2-*Trichloroethyl* 6β-*Hydroxymethyl*-6α-(4-*methoxyphenyl*)*penicillanate* (**16**).—Sodium borohydride (5 mg, 0.125 mmol) was added to a solution of the 6-formylpenicillanate (**14**) (50 mg, 0.107 mmol) in aqueous dioxane (15 ml). After 30 min the mixture was extracted into chloroform. Preparative t.l.c. using ethyl acetate and light petroleum as eluant gave 2,2,2-*trichloroethyl* 6β-*hydroxymethyl*-6α-(4-*methoxyphenyl*)*penicillanate* (**16**) (27 mg, 53%), m.p. 105—107 °C (from ethyl acetate–light petroleum) (Found: M^+, 467.0128. $C_{18}H_{20}NO_5S^{35}Cl_3$ requires *M*, 467.0125; $\nu_{max.}$($CHCl_3$) 1 780 and 1 760 cm^{-1}; δ_H($CDCl_3$) 1.60 and 1.78 (each 3 H, s, Me), 1.96 (1 H, br s, OH), 3.81 (3 H, s, OMe), 4.04 (1 H, dd, *J* 4, 12 Hz, *H*CHOH), 4.24 (1 H, dd, *J* 8, 12 Hz, HC*H*OH), 4.63 (1 H, s, 3-H), 4.69 and 4.83 (each 1 H, d, *J* 12 Hz, $HCHCCl_3$), 5.57 (1 H, s, 5-H), and 6.9—7.3 (4 H, m, ArH); δ_C($CDCl_3$) 26.87, 32.00, and 55.35 (each q, Me), 64.45 (t, CH_2OH), 64.64 (s, 6-C), 67.87 (s, 2-C), 68.25 (d, 5-C), 72.09 (d, 3-C), 74.87 (t, CH_2CCl_3), 94.01 (s, CCl_3), 114.43 and 127.95 (d, ArC), 128.58 and 159.44 (s, ArC), and 166.10 and 172.61 (each s, C=O). Also isolated was the oxazinone (**5**) (10 mg, 20%).

(6R)-2,2,2-*Trichloroethyl*-6-(4-*methoxyphenyl*)-6-*phenyliminomethylpenicillanate* (**17**).—Freshly distilled aniline (24 mg, 0.26 mmol) was added to a mixture of 6-formylpenicillanate (**14**) (60 mg, 0.13 mmol) in dichloromethane (10 ml) and anhydrous $MgSO_4$ (1 g). After 2 h at room temperature, the mixture was filtered, and the filtrate concentrated under reduced pressure. Preparative t.l.c. using ethyl acetate–light petroleum (1:1), as eluant gave the *imine* (**17**) (30 mg, 50%), m.p. 141—142 °C (from ethyl acetate–light petroleum); $\nu_{max.}$($CHCl_3$) 1 770, 1 720, and 1 660 cm^{-1}; δ_H($CDCl_3$) 1.58 and 1.73 (each 3 H, s, Me), 3.81 (3 H, s, OMe), 4.69 (1 H, s, 3-H), 4.71 and 4.86 (each 1 H, d, *J* 12 Hz, HC*H*CCl_3), 5.67 (1 H, s, 5-H), 6.94 and 7.44 (each 2 H, m, ArH), 7.1—7.4 (5 H, m, ArH), and 7.94 (1 H, s, HC=N); δ_C($CDCl_3$) 26.41, 31.28, and 55.37 (each q, Me), 64.13 (s, 2-C), 68.63 (d, 5-C), 71.92 (s, 6-C), 73.16 (d, 3-C), 74.86 (t, CH_2CCl_3), 94.06 (s, CCl_3), 114.70, 120.84, 126.28, 127.22, 127.99, 129.03, 151.06, and 159.71 (Ar C), 158.72 (d, C=N), and 166.25 and 170.60 (s, C=O). The oxazinone (**5**) (3 mg, 4%) was also obtained.

Enolate Reactions of 6-*Acetylpenicillanate* (**18**).—*With acetyl chloride.* 6-Diazopenicillanate (**1**) (0.5 g, 1.39 mmol) was dissolved in dichloromethane, and the solution cooled to 10—14 °C. Acetaldehyde (*ca.* 2 ml) was added, followed by a few crystals of anhydrous zinc chloride. After being stirred for 35 min, the reaction mixture was washed with aqueous orthophosphoric acid, and dried ($MgSO_4$). Concentration under reduced pressure gave the 6-acetylpenicillanate (**18**), δ_H($CDCl_3$) 1.57 and 1.7 (each 3 H, s, Me), 2.30 (3 H, s, $COCH_3$), 4.28 (1 H, d, *J* 2 Hz, 6-H), 4.58 (1 H, s, 3-H), 4.80 (2 H, s, CH_2CCl_3), and 5.65 (1 H, d, *J* 2 Hz, 5-H). The crude acylpenicillanate was dissolved in dichloromethane (20 ml), cooled to 0—5 °C, and acetyl chloride (0.1 ml, 1.39 mmol) was added. After 5 min, a solution of triethylamine (140 mg, 1.39 ml) in dichloromethane (2 ml) was added dropwise and the whole was then stirred at 0—5 °C for 1 h. The mixture was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography on silica, using ethyl acetate–light petroleum (1:9) as eluant, gave three fractions. The first eluted product was identified as (6Z)-2,2,2-*trichloroethyl* 6-(1-*acetoxyethylidene*)*penicillanate* (**19**) (204 mg, 35%), a colourless oil (Found: M^+, 414.9833. $C_{14}H_{16}{}^{35}Cl_3NO_5S$ requires *M*, 414.9814); $\nu_{max.}$($CHCl_3$) 1 780, 1 760, 1 420, 1 375, and 1 180 cm^{-1}; δ_H($CDCl_3$) 1.54 and 1.65 (each 3 H, s, Me), 2.21 (3 h s, CH_3CO), 2.25 [3 H, d, *J* 1.1 Hz, $CH_3C(OCOCH_3)$], 4.58 (1 H, s, 3-H), 4.74 and 4.84 (each 1 H, d, *J* 12 Hz, CH_2CCl_3), and 5.72 (1 H, q, *J* 1.1 Hz, 5-H); δ_C($CDCl_3$) 18.02, 20.94, 26.33, and 32.18 (each q, CH_3), 64.33 (s, 2-C), 67.42 (d, 3-C), 69.84 (d, 5-C), 74.90 (t, CH_2CCl_3), 94.16 (s, CCl_3), 127.55 (s, 6-C), 148.56 [s, $CH_3C(OCOCH_3)$], and 166.68, 166.88, and 168.82 (each s, 7-C, $CO_2CH_2CCl_3$, and CH_3CO_2); *m/z* 415 (M^+). The second eluted product, a pale yellow oil, was identified as (6E)-2,2,2-*trichloroethyl* 6-(1-*acetoxyethylidene*)-*penicillanate* (**20**) (23 mg, 4%) (Found: M^+, 414.9815. $C_{14}H_{16}{}^{35}Cl_3NO_5S$ requires *M*, 414.9814); $\nu_{max.}$($CHCl_3$) 1 780, 1 760, 1 720, 1 375, and 1 180 cm^{-1}; δ_H($CDCl_3$) 1.55 and 1.63 (each 3 H, s, Me), 2.01 [3 H, s, $CH_3C(OCOCH_3)$], 2.24 (3 H, s, $OCOCH_3$), 4.60 (1 H, s, 3-H), 4.77 and 4.80 (each 1 H, d, *J* 12 Hz, $HCHCCl_3$), and 5.80 (1 H, s, 5-H); *m/z* 414 (M^+). The third eluted product was identified as (3S)-2,2,2-*trichloroethyl* 4,6-*diacetyl*-2,2-*dimethyl*-7-*oxo*-2,3,4,7-*tetrahydro*-1,4-*thiazepine*-3-*carboxylate* (**21**) (102 mg, 18%), a colourless oil (found: M^+, 414.9814. $C_{14}H_{16}{}^{35}Cl_3NO_5S$ requires *M*, 414.9814); $\nu_{max.}$($CHCl_3$) 1 760, 1 720, 1 690, 1 620, and 1 590 cm^{-1}; δ_H($CDCl_3$) 1.60 and 1.76 (each 3 H, s, Me), 2.37 and 2.58 (each 3 H, s, $COCH_3$), 4.64 and 4.84 (each 1 H, d, *J* 12 Hz, $HCHCCl_3$), 5.83 (1 H, d, *J* 1 Hz, 3-H), and 8.39 (1 H, d, *J* 1 Hz, 5-H); *m/z* 415 (M^+).

With ethyl chloroformate. Crude 6α-acetylpenicillanate (**12**) from 6-diazopenicillanate (**1**) (220 mg, 0.6 mmol) was treated with ethyl chloroformate (0.68 ml, 0.65 mmol) and triethylamine (66 mg, 0.65 mmol) in dichloromethane (10 ml) as described above. Two products were isolated by chromatography using ethyl acetate–hexane (1:9), as eluant. The first eluted product was identified as (6Z)-2,2,2-*trichloroethyl* 6-(1-*ethoxycarbonyloxyethylidene*]*penicillanate* (**22**) (31 mg, 11%) a pale yellow oil (Found: M^+, 444.9920. $C_{15}H_{18}{}^{35}Cl_3NO_6S$ requires *M*, 444.9918); $\nu_{max.}$($CHCl_3$) 1 785, 1 760, 1 710, 1 445, and 1 370 cm^{-1}; δ_H($CDCl_3$) 1.37 (3 H, t, *J* 7.3 Hz, CH_3CH_2), 1.54, 1.65, and 2.30 (each 3 H, s, Me), 4.29 (2 H, q, *J* 7.3 Hz, CH_3CH_2), 4.59 (1 H, s, 3-H), 4.69 and 4.89 (each 1 H, d, *J* 12 Hz, CH_2CCl_3), and 6.21 (1 H, s, 5-H); δ_C($CDCl_3$) 14.09, 17.63, 26.30, and 32.29 (each q, Me), 64.29 (s, 2-C), 65.55 (t, CH_3CH_2), 67.44 and 69.88 (each d, 3-C and 5-C), 74.88 (t, CH_2CCl_3), 94.12 (s, CCl_3), 126.92 (s, 6-C), 148.21 [s, $CH_3C(OCO_2Et)$], 150.82 (s, OCO_2), 166.63 (s, 7-C), and 168.77 (s, $CO_2CH_2CCl_3$); *m/z* 445 (M^+).

The second eluted material was identified as (3S)-2,2,2-*trichloroethyl* 6-*acetyl*-4-*ethoxycarbonyl*-2,3,4,7-*tetrahydro*-2,2-*dimethyl*-7-*oxo*-1,4-*thiazepine*-3-*carboxylate* (**23**) (61 mg, 22%), m.p. 104—105 °C from CH_2Cl_2–light petroleum (Found: $M^+ + 1$, 445.9974. $C_{15}H_{19}{}^{35}Cl_3NO_6S$ requires M, 445.9998); $\nu_{max.}$($CHCl_3$) 1 750, 1 720, 1 690, 1 620, and 1 580 cm^{-1}; δ_H($CDCl_3$) 1.40 (3 H, t, J 7 Hz, CH_3CH_2), 1.68, 1.78, and 2.39 (each 3 H, s, Me), 4.42 (2 H, q, J 7 Hz, CH_3CH_2), 4.69 and 4.89 (each 1 H, d, J 12 Hz, $HCHCCl_3$), 5.58 (1 H, d, J 1.4 Hz, 3-H), and 8.67 (1 H, d, J 1.4 Hz, 5-H); δ_C($CDCl_3$) 14.19, 28.04, 29.41, and 30.22 (each q, Me), 44.38 (s, 2-C), 66.06 (t, CH_3CH_2), 69.25 (d, 3-C), 75.34 (t, CH_2CCl_3), 93.84 (s, CCl_3), 121.80 (s, 6-C), 141.26 (d, 5-C), and 153.62, 165.21, 190.44, and 196.56 (each s, C=O); m/z 446 ($M^+ + 1$).

With benzeneselenenyl chloride. Benzeneselenenyl chloride (133 mg, 0.7 mmol) was added to 6α-acetylpenicillanate (**18**) (260 mg, 0.7 mmol) in dichloromethane (5 ml). The mixture was cooled to 0—5 °C when triethylamine (70 mg, 0.7 mmol) in dichloromethane (2 ml) was added. The red solution was stirred at 0—5 °C for 30 min, by which time it had turned to a dark yellow. It was then washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography on silica using ethyl acetate–light petroleum as eluant (1:19) gave a 5:1 mixture of the selenides (**24**) and (**25**) (137 mg, 37%). Crystallization gave 2,2,2-*trichloroethyl* 6β-*acetyl*-6α-*phenylselenopenicillanate* (**24**), m.p. 84—85 °C (from dichloromethane–light petroleum) (Found: M^+, 528.9233. $C_{18}H_{18}{}^{35}Cl_3NO_4S^{80}Se$ requires M, 528.9184); $\nu_{max.}$($CHCl_3$) 1 780, 1 760, and 1 700 cm^{-1}; δ_H($CDCl_3$) 1.51 and 1.63 (each 3 H, s, Me), 2.40 (3 H, s, CH_3CO), 4.46 (1 H, s, 3-H), 4.71 and 4.82 (each 1 H, d, J 12 Hz, $HCHCCl_3$), 5.39 (1 H, s, 5-H), 7.3—7.7 (5 H, m, ArH); m/z 529 (M^+).

Trapping of 6-(4-*Nitrobenzoyl*)*penicillanate* (**11**).—Tin(IV) chloride (6 drops) was added to 6-diazopenicillanate (**1**) (750 mg, 2.1 mmol) and 4-nitrobenzaldehyde (310 mg, 2.1 mmol) in dichloromethane (30 ml) at room temperature. After a few minutes the solution was washed with orthophosphoric acid (10%; 15 ml), dried ($MgSO_4$), and filtered. The solution was then cooled to 0—5 °C, and acetyl chloride (0.15 ml, 2.1 mmol) was added. After 5 min at 0—5 °C, a solution of triethylamine (210 mg, 2.1 mmol) in dichloromethane (2 ml) was added dropwise. After 30 min, the mixture was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed on silica using ethyl acetate–light petroleum (1:9) as eluant. Early fractions contained the spiro epoxide (**4**) and the oxazinone (**6**); later fractions were found to contain the enol esters (**26**) and (**27**) (264 mg, 24%), and the thiazepine (**28**) (88 mg, 8%). The enol esters were separated by repeated chromatography on silica using dichloromethane as eluant. The first eluted material was identified as (Z)-2,2,2-*trichloroethyl* 6-[*acetoxy*-(4-*nitrophenyl*)*methylene*]*penicillanate* (**26**) (151 mg, 14%), a pale yellow oil (Found: M^+, 521.9858. $C_{19}H_{17}{}^{35}Cl_3N_2O_7S$ requires M, 521.9820); $\nu_{max.}$($CHCl_3$) 1 780, 1 760, 1 520, and 1 350 cm^{-1}; δ_H($CDCl_3$) 1.59 and 1.68 (each 3 H, s, Me), 2.38 (3 H, s, $COCH_3$), 4.68 (1 H, s, 3-H), 4.78 and 4.87 (each 1 H, d, J 12 Hz, $HCHCCl_3$), 5.81 (1 H, s, 5-H), and 8.09 and 8.29 (each 2 H, m, ArH); δ_C($CDCl_3$) 20.62, 26.20, and 32.32 (each q, CH_3), 64.71 (s, 2-C), 66.42 and 70.35 (each d, 5-C and 3-C), 75.00 (t, CH_2CCl_3), 94.09 (s, CCl_3), 123.91 and 128.12 (each d, ArC), 133.24 (s, 6-C), 145.06 (s, 8-C), 136.78 and 149.05 (each s, ArC), and 165.58, 166.24, and 167.12 (each s, C=O); m/z 522 (M^+). The second eluted material was identified as (E)- 2,2,2-*trichloroethyl* 6-[*acetoxy*(4-*nitrophenyl*)-*methylene*]*penicillanate* (**27**) (22 mg, 2%), a white foam (Found: M^+, 521.9833. $C_{19}H_{17}{}^{35}Cl_3N_2O_7S$ requires M, 521.9820); $\nu_{max.}$($CHCl_3$) 1 780, 1 760, 1 680, 1 600, 1 520, and 1 350, cm^{-1}; δ_H($CDCl_3$) 1.59 and 1.68 (each 3 H, s, Me), 2.42 (3 H, s, CH_3CO), 4.72 (1 H, s, 3-H), 4.80 and 4.84 (each 1 H, d, J 12 Hz, $HCHCCl_3$), 6.14 (1 H, s, 5-H), and 7.66 and 8.31 (each 2 H, m, ArH); m/z 522 (M^+). The third product was identified as (3S)-2,2,2-*trichloroethyl* 4-*acetyl*-2,3,4,7-*tetrahydro*-2,2-*dimethyl*-6-(4-*nitrobenzoyl*)-7-*oxo*-1,4-*thiazepine*-3-*carboxylate* (**28**) (88 mg, 8%), a pale yellow oil (Found: M^+, 521.9807. $C_{19}H_{17}{}^{35}Cl_3N_2O_7S$ requires M, 521.9820); $\nu_{max.}$($CHCl_3$) 1 760, 1 720, 1 675, 1 600, 1 520, and 1 350 cm^{-1}; δ_H($CDCl_3$) 1.81 and 1.88 (each 3 H, s, Me), 2.63 (3 H, s, CH_3CO), 4.72 and 4.90 (each 1 H, d, J 12 Hz, $HCHCCl_3$), 6.03 (1 H, d, J 1 Hz, 3-H), 7.82 and 8.27 (each 2 H, m, Ar H), and 8.08 (1 H, d, J 1 Hz, 5-H); δ_C($CDCl_3$) 22.21, 28.44, and 29.46 (each q, Me), 44.61 (s, 2-C), 66.14(d, 3-C), 75.51 (t, CH_2CCl_3), 93.80 (2, CCl_3), 121.27 (s, 6-C), 123.66 and 129.22 (each d, ArC), 140.61 (d, 5-C), 143.54 and 149.79 (each s, ArC), and 164.94, 171.14, 189.72, and 192.46 (each s, C=O); m/z 522 (M^+).

Table 1. Atom co-ordinates ($\times 10^4$) for compound (**5**)

Atom	x	y	z
S(1)	−602(2)	6 752(1)	8 384(1)
C(2)	2 159(7)	6 886(2)	8 594(2)
C(3)	2 977(6)	6 078(2)	8 677(2)
N(4)	1 341(5)	5 656(2)	9 026(2)
C(5)	−732(6)	5 853(2)	8 829(2)
O(6)	−1 986(4)	5 867(2)	9 481(2)
C(7)	−1 820(7)	5 205(2)	9 851(2)
C(8)	−178(6)	4 761(2)	9 833(2)
C(9)	1 702(6)	5 051(2)	9 469(2)
O(9)	3 444(4)	4 827(2)	9 575(2)
C(10)	−91(6)	4 042(2)	10 246(2)
C(11)	−1 369(7)	3 893(2)	10 845(2)
C(12)	−1 295(7)	3 220(2)	11 217(2)
C(13)	75(7)	2 671(2)	11 001(2)
C(14)	1 336(7)	2 801(2)	10 412(2)
C(15)	1 241(7)	3 471(2)	10 040(2)
O(16)	21(5)	2 022(2)	11 406(2)
C(17)	1 477(9)	1 465(3)	11 224(3)
C(18)	3 660(7)	5 716(2)	7 959(2)
O(18)	5 412(5)	5 679(2)	7 755(2)
O(19)	2 068(5)	5 460(2)	7 560(2)
C(20)	2 506(8)	5 084(3)	6 876(2)
C(21)	1 382(7)	4 346(2)	6 876(2)
C(22)	2 423(10)	7 292(3)	9 326(3)
C(23)	3 154(8)	7 309(2)	7 954(3)
Cl(1)	−1 289(2)	4 490(1)	6 971(1)
Cl(2)	2 247(3)	3 771(1)	7 590(1)
Cl(3)	1 869(3)	3 911(1)	6 021(1)

Oxidation of the Oxazinone (**5**).—*m*-Chloroperoxybenzoic acid (163 mg, 0.94 mmol) was added to a solution of the oxazinone (**5**) (400 mg, 0.86 mmol) in chloroform (50 ml) at room temperature. After 1 h the mixture was concentrated under reduced pressure, and the residue chromatographed on silica, using chloroform as eluant. The first fractions off the column crystallized on concentration to give (2S,5S)-2,2,2-*trichloroethyl*-4-*formyltetrahydro*-2-(4-*methoxyphenyl*)-6,6-*dimethyl*-3-*oxo*-1,4-*thiazine*-5-*carboxylate* (**29**) (142 mg, 36%), m.p. 160—162 °C (from chloroform); $\nu_{max.}$($CHCl_3$) 1 760, 1 720, and 1 690 cm^{-1}; δ_H($CDCl_3$) 1.64 and 1.72 (each 3 H, s, Me), 3.80 (3 H, s, OMe), 4.79 and 5.02 (each 1 H, d, J 12 Hz, $HCHCCl_3$), 5.01 (1 H, s, 5-H), 5.17 (1 H, s, 2-H), 6.88 and 7.4 (each 2 H, m, ArH), and 9.53 (1 H, s, N–CHO); δ_C($CDCl_3$) 26.46 and 28.80 (each q, Me), 40.98 (s, 6-C), 47.12 (d, 2-C), 55.31 (q, OMe), 65.73 (d, 5-C), 75.36 (t, CH_2CCl_3), 94.02 (s, CCl_3), 114.40 and 130.82 (each d, ArC), 127.18 and 159.86 (each s, ArH), 163.08, 167.07, and 169.78 (each s, C=O).

Table 2. Atom co-ordinates ($\times 10^4$) for compound (**29**)

Atom	*x*	*y*	*z*
S(1)	8 768(2)	6 554(1)	8 757(1)
C(2)	9 818(6)	4 983(4)	8 940(1)
C(3)	8 296(6)	4 073(4)	9 135(1)
N(4)	7 496(5)	4 598(4)	9 587(1)
C(5)	6 960(7)	5 926(4)	9 651(2)
O(5)	5 933(5)	6 198(4)	9 990(1)
C(6)	7 702(6)	7 037(4)	9 335(2)
C(7)	7 032(7)	3 659(5)	9 942(2)
O(8)	7 329(6)	2 498(4)	9 898(1)
C(9)	11 228(7)	5 171(6)	9 338(2)
C(10)	10 713(7)	4 414(5)	8 477(2)
C(11)	6 745(5)	3 808(4)	8 783(1)
O(11)	5 297(4)	4 317(3)	8 806(1)
O(12)	7 140(4)	2 879(3)	8 445(1)
C(13)	5 702(7)	2 607(5)	8 102(2)
C(14)	6 374(8)	1 668(5)	7 713(2)
Cl(1)	6 903(2)	84(1)	7 961(1)
Cl(2)	4 610(3)	1 480(2)	7 285(1)
Cl(3)	8 309(3)	2 315(2)	7 418(1)
C(15)	6 295(6)	8 077(4)	9 213(1)
C(16)	4 773(6)	7 700(4)	8 948(2)
C(17)	3 429(6)	8 601(5)	8 830(2)
C(18)	3 627(7)	9 908(4)	8 972(2)
C(19)	5 119(7)	10 312(4)	9 227(2)
C(20)	6 455(6)	9 385(4)	9 352(1)
O(21)	2 399(5)	10 899(3)	8 860(1)
C(22)	811(8)	10 504(7)	8 595(3)

Crystal Data.—Compound (**5**) $C_{18}H_{18}Cl_3NO_5S$, M = 466.8 orthorhombic, a = 6.502 (1), b = 17.838(2), c = 18.036(2) Å, U = 2 092 Å^3, μ(Cu-K_α) = 52 cm^{-1}, λ = 1.54178 Å, space group $P2_12_12_1$, Z = 4, D_c = 1.49 g cm^{-3}, F(000) = 952. Approximate crystal dimensions 0.15 × 0.18 × 0.30 mm; compound (**29**) $C_{17}H_{18}Cl_3NO_5S$ M = 454.7, orthorhombic, a = 7.382(2), b = 10.002(3), c = 27.215(7) Å, U = 2 009 Å^3, μ(Cu-K_α) = 54 cm^{-1}, λ = 1.541 78 Å, space group $P2_12_12_1$, Z = 4, D_c = 1.51 g cm^{-3}, F(000) = 936. Approximate crystal dimensions: 0.05 × 0.10 × 0.15 mm.

Data Collection and Processing.—Compound (**5**) 1 565 independent observed reflections [$|F_o| > 3\,\sigma(|F_o|)$, $\theta < 58°$] and (**29**) 1 524 independent observed reflections [$|F_o| > 3\,\sigma(|F_o|)$, $\theta < 58°$] were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromater) and using ω-scans.

Structured Analysis and Refinement.—Both structures were solved by direct methods and all the non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters [U(H) = 1.2U_{eq}(C)], and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. Refinement was by block-cascade full-matrix least-squares and converged to give for (**5**) R = 0.036, R_w = 0.039 ($w^{-1} = \sigma^2(F) + 0.0005F^2$) and for (**29**) R = 0.043, R_w = 0.047 ($w^{-1} = \sigma^2(F) + 0.0014F^2$). Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[13]

Fractional atomic co-ordinates for the non-hydrogen atoms for compounds (**5**) and (**29**) are given in Tables 1 and 2 respectively. Bond lengths, bond angles, the fractional co-ordinates of the hydrogen atoms, the isotropic thermal parameters and the anisotropic thermal parameters for the non-hydrogen atoms for compounds (**5**) and (**29**) are available on request from the Cambridge Crystallographic Data Centre.*

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* See Instructions for Authors (1986), para 5.6.3, in *J. Chem. Soc., Perkin Trans. 1*, 1986, Issue 1.

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