Stereospecific Transformations of Steroidal 2,3-Aziridines into Substituted Amino-thiols and Ring-A Fused Heterocycles

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1'-Acetyl-2β,3β-dihydro- and 1'-acetyl-2α,3α-dihydro-androst-2-eno[2,3-*b*]azirin-17-one reacted with thiobenzoic *S*-acid to give the expected *trans*-diaxial ring-opened products, together with unexpected *N*-benzoylaziridines arising from transacylation. A mixed thioanhydride is postulated in a reaction pathway leading to the latter products.

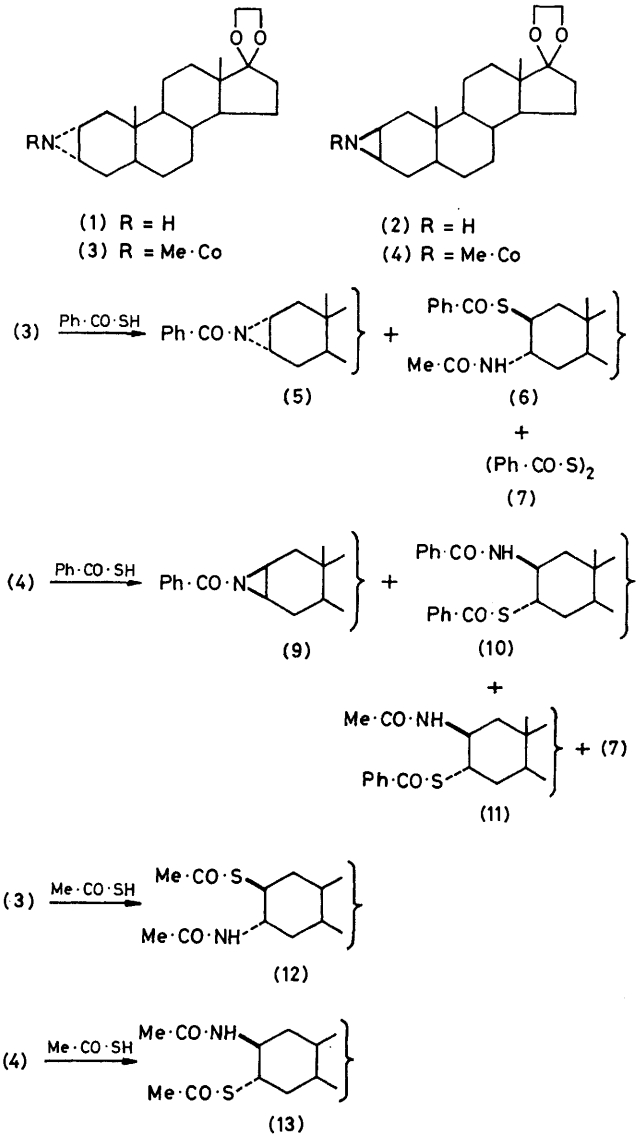
Classical *trans*-diaxial ring-opening and cyclization concepts were exemplified in ring-expansion reactions of aziridine derivatives to give chemospecific and stereoselective routes to a range of ring-A fused thiazolines and ring-A fused imidazo[2,1-*b*]thiazolines.

STEROIDAL 2α,3α- and 2β,3β-aziridines have been exploited in stereospecific syntheses of a range of isomeric vicinal amino-alcohols of pharmacological interest as antiarrhythmics.[1] *trans*-Diaxial openings of (1) and (2) led to *trans*-amino-alcohols, whereas *N*-acylated aziridines were ring-expanded to *cis*-2α,3α- and -2β,3β-oxazolines which in turn yielded *cis*-amino-alcohols. We now report complementary studies in which ring-opening reactions with *S*-thioacids have been studied, and *N*-thioacylated aziridines have been stereospecifically converted into a range of ring-A fused heterocycles.

Reactions with S-*Thioacids: Transacylations.*—The *N*-acetyl 2α,3α-aziridine (3) [1] when treated with thiobenzoic *S*-acid gave, together with dibenzoyl disulphide (7), the unexpected transacylated *N*-benzoyl 2α,3α-aziridine (5) [1,†] as the major product and the expected *trans*-diaxial ring-opened product (6). In (6) the diequatorial stereochemistry for H-2 and H-3 was readily assigned from the half-band widths [1] in the n.m.r. spectrum ($W_{\frac{1}{2}}$ 12 Hz).

The probable mechanism for the formation of (5) is depicted in Scheme 1. Acyl aziridines possess little amide character,[2] and the thiobenzoic acid readily attacks the acyl group with formation of a mixed thioanhydride and free aziridine (1). Attack by (1) on the benzoyl unit leads to (5). It was shown that (6) was not an intermediate in the formation of (5), by subjecting the former to similar reaction conditions, thereby precluding an alternative multi-step pathway to (5). To establish the possible intermediacy of the mixed thioanhydride, (8) was prepared [3] and shown to react with the aziridine (1) to give two products, the less polar, minor product being (5) and the major product being the *N*-acetylaziridine (3). Although rigorous studies of the thermodynamic equilibria in these reactions were not performed, the mixed thioanhydride is probably implicated as shown in Scheme 1.

The reaction of thiobenzoic *S*-acid with the *N*-acetyl-2β,3β-aziridine (4) gave a complex mixture containing dibenzoyl disulphide (7), a transacylation product (9), 2β-benzamido-3α-thiobenzoate (10), and the expected

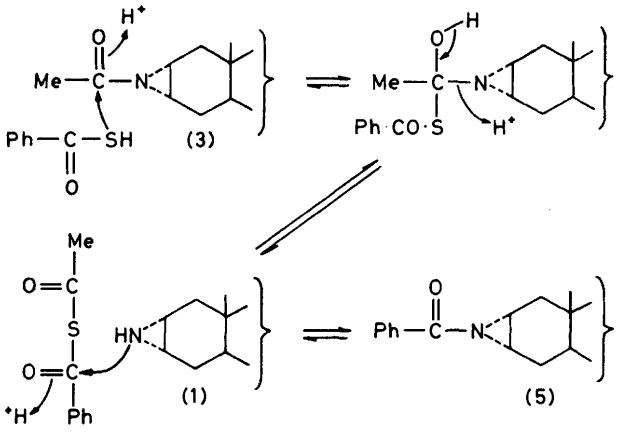


trans-diaxial ring-opened product (11). ‡ Formation of (9) parallels the rearrangement in Scheme 1, and (10),

† All steroids were obtained as 17-one ethylene acetals unless otherwise stated.

‡ The elemental composition and spectroscopic data for (11) were in accord with the structure shown, with the exception of an apparent hydroxy-group in the i.r. and n.m.r. spectra which could not readily be explained. See Experimental section.

which results from ring-opening of (9) by thiobenzoic *S*-acid, reflects the ease of opening of β-oriented aziridines with respect to their α-analogues. The stereo-



SCHEME 1

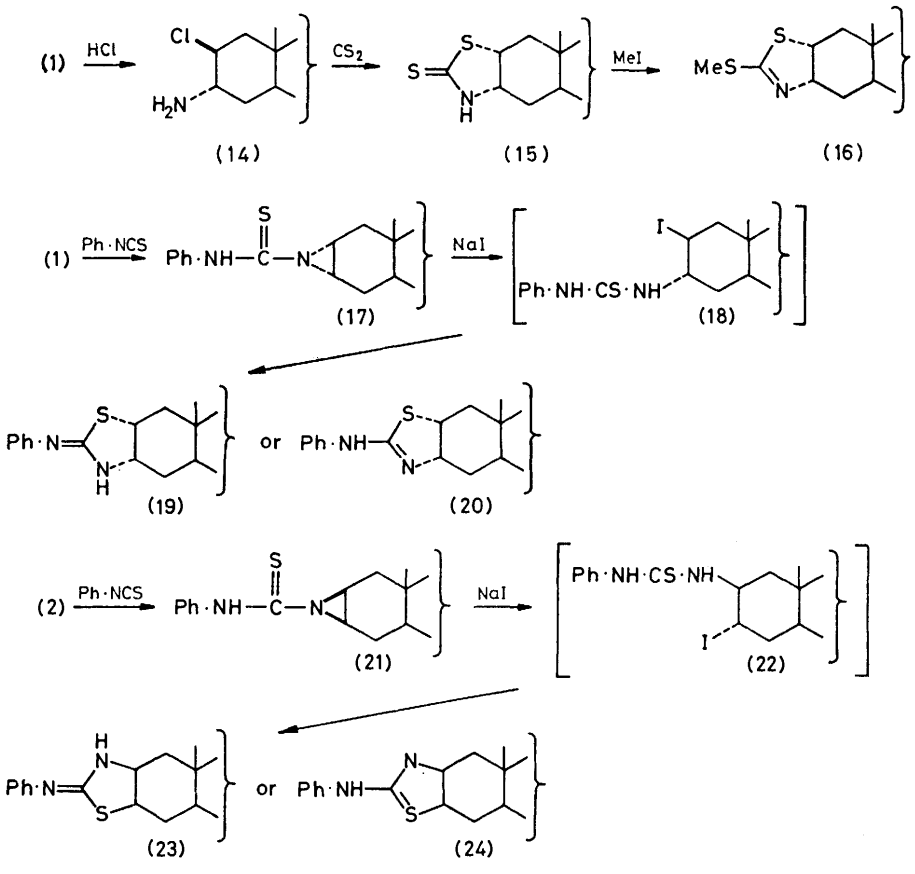
chemical constraints implicit in the ring-opening of steroidal 2,3-epoxides have been reviewed [4] and nucleophilic attack at C-3 for the β-ring is considered to be relatively unhindered, whereas attack at C-2 of the α-ring is sterically inhibited.

Reaction of thioacetic *S*-acid with *N*-acetylaziridines was also investigated, the α-isomer (3) giving one major product shown to be the expected 2β-acetylthio-3α-acetamide (12), and the β-isomer (4) also giving a normal *trans*-diaxial ring-opened product (13). Mass spectroscopic investigations of the thioacid products obtained in all the foregoing studies resulted in diagnostically useful fragmentation modes which will be reported in detail elsewhere.

Stereospecific Routes to Ring-A Fused Thiazolines and Related Heterocycles.—Heterocycles fused to steroids have attracted a great deal of attention because of the resulting range of pharmacological behaviour.[5] Consequently we have utilised steroidal 2,3-aziridines in the stereospecific synthesis of a range of thiazoline and benzothiazole ring-A fused steroids.

In a preliminary approach, the aziridine (1) was transformed into the 3α-amino-2β-chloro-steroid (14) [1] which was treated with carbon disulphide according to a method developed by Ponsold [6] to give (15). In the n.m.r. spectrum H-2 and H-3 were respectively axial and equatorial (a broad doublet and diffuse singlet, $W_{\frac{1}{2}}$ 16 and 7 Hz, confirming formation of a 2,3-*cis*-fused heterocycle). Methylation of (15) with methyl iodide–sodium hydrogen carbonate gave the *S*-methyl product (16).

Alternative routes to thiazolines from both the α- and β-aziridines (1) and (2) involved initial *N*-thioacylation with phenyl isothiocyanate. Thus (1) gave an unstable thiocarbamoyl aziridine (17), the spectroscopic characteristics of which were in accord with the assigned structure. Ring expansion of (17) by reaction with



sodium iodide in acetone gave, by *trans*-diaxial ring-opening, a 2β-iodo-intermediate (18) which spontaneously cyclized to the thiazolidine (19), or its thiazoline tautomer (20).[6] (The possible alternative imidazoline cyclization product was not obtained, in keeping with precedent.[7]) Comparison of the n.m.r. characteristics of H-2 and H-3 with those of the thiazoline (16) and the thiazolidine-thione (15) showed a greater similarity to the former tautomer, favouring assignment of structure (20) in solution.

Similarly, the β-aziridine (2) gave the thiocarbamoyl aziridine (21) which was transformed by sodium iodide *via* the 3α-iodo-intermediate (22) into the 2β,3β-thiazolidine (23) or its tautomer (24). In the reactions of the 2α,3α- and 2β,3β-thiocarbamoylaziridines the classical *trans*-diaxial ring-opening constraints are therefore exemplified in the formation of 2,3-*trans*-substituted intermediates which lead to the 2α,3α- and 2β,3β-*cis*-fused heterocycles.

In an extrapolation of this stereospecific strategy, 2-chlorobenzothiazole was treated with (1) to give the *N*-(benzothiazol-2-yl)aziridine (25). Treatment with sodium iodide, as for (17) and (21), did not in this case afford the ring-expanded product (26). However, more forcing reaction with triethylamine hydrochloride[8] gave the 3α-amino-2β-chloro-ring-opened product (27) which did not undergo further reaction.

The 2β,3β-aziridine (2) was also transformed into an *N*-(benzothiazol-2-yl)aziridine (28) in a reaction which is extremely slow compared to that of (1), reflecting adverse steric interactions in this case. Reaction of (28) with triethylamine hydrochloride gave, as a more polar product, the target heterocycle (30). H-2 and H-3 were apparent in the n.m.r. spectrum as equatorial and axial protons respectively, pointing to a 2β,3β-fused heterocycle. Presumably the intermediate 3α-amino-2β-chloro-derivative (29) is involved.

It is of interest that the reaction of (25) with triethylamine hydrochloride stops at the 3α-amino-2β-chloro-product (27) whereas the isomeric aziridine (28) is relayed through an unisolable chloroamine to a ring-expanded heterocycle (30). In the case of the intermediate (29) the enhanced reactivity is in part due to steric decompression alleviating the 1,3-diaxial interaction between the C-10 methyl and the bulky 2β-amino-derivative thus facilitating ring closure to the ring-closed product (30).

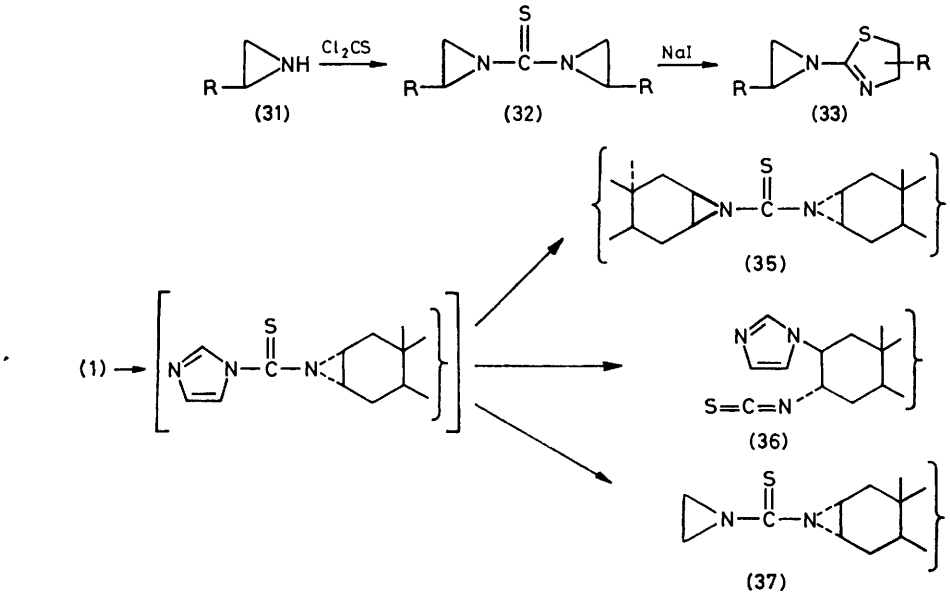
Alternative synthetic approaches to ring-A fused heterocycles were based on *N*-thioacyl aziridines, employing methods related to those of Tomalia,[9] who prepared aziridin-2-ylthiazolines (33) from aziridines (31) and thiophosgene, followed by ring-expansion of the bisaziridine thiocarbonyl intermediate (32). Rather than thiophosgene, 1,1′-thiocarbonyldi-imidazole[10] was used in our studies.

Because of the possibility of formation of thioacyl bisaziridines in these reactions, compound (35) was synthesized and characterized prior to further investigations, by adding the thioacylating agent to an equimolar quantity of the α-aziridine (1).

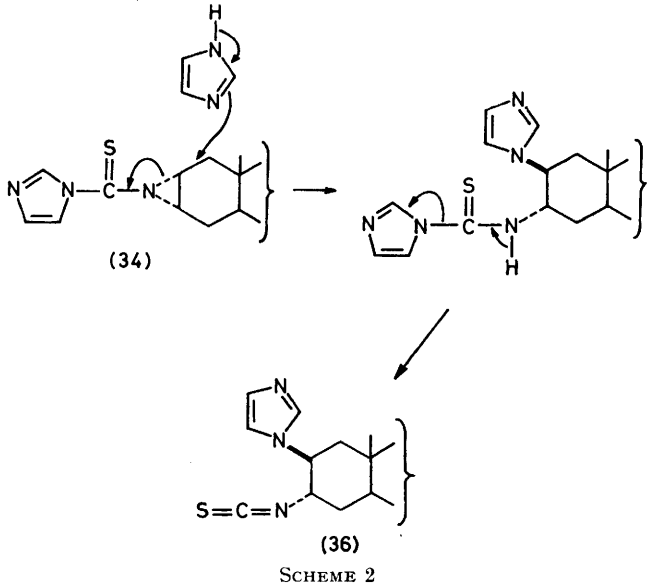
Reaction of the α-aziridine with excess of 1,1′-thiocarbonyldi-imidazole gave a less polar product (t.l.c. analysis) which was gradually transformed into a single, more polar product, shown to be the unexpected isothiocyanate (36). In the i.r. spectrum an intense absorption appeared at 2 012 cm^{-1} and in the n.m.r. spectrum an imidazole group was present (δ 7.01, 7.13, and 7.59) together with equatorial 2-H and 3-H protons (overlapping, δ 4.47, $W_{\frac{1}{2}}$ *ca.* 10 Hz). Additionally, 10-Me was at high field (δ 0.63) owing to anisotropic shielding by the axial 2β-imidazole. Assuming that the non-polar intermediate in the reaction was (34), it is probable that *trans*-diaxial attack by imidazole, as depicted in Scheme 2, leads to a transient thiourea which then eliminates imidazole, as in the case of simpler imidazolythioamides which give isothiocyanates.[10]

Attempts to isolate (34) were unsuccessful, and it was therefore decided to trap it. At low temperature, the reaction was repeated and a further molar equivalent of the α-aziridine (1) added, resulting in formation of the

bis-steroid (35). This showed that the intermediate (34) was being formed, and had to be trapped rapidly to avoid formation of (36). In a further trapping experiment (34) was generated *in situ* and aziridine [11] was added. Immediate work-up gave a product which, though unstable, was adequately characterized spectroscopically as the aziridinylthiocarbonyl α-aziridine (37).



The i.r. spectrum contained two medium intensity bands at 809 and 783 cm^{-1} which are due to C–H deformation modes of aziridine protons and the n.m.r. spectrum

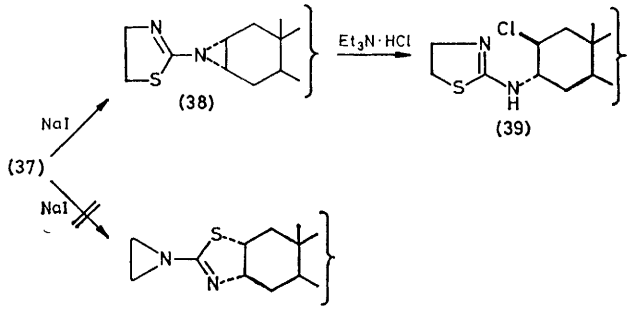


SCHEME 2

showed four aziridinyl protons as a singlet at δ 2.53 and H-2 and H-3 as a characteristic multiplet at δ 2.88.

Ring-expansion of (37) was of immediate interest because four isomeric products were theoretically possible, depending upon which aziridine undergoes initial ring-expansion. Thus investigations using sodium iodide–acetonitrile afforded a single product shown to be (38). (Scheme 3.) Important spectroscopic features included a fragment ion at *m/e* 388 (*M* — 28) in the mass spectrum, indicative of a 2,3-fused steroidal aziridine.[12] In the n.m.r. spectrum H-2 and H-3 appeared at δ 2.60 as a characteristic multiplet and the thiazoline protons appeared as a complex ABMN multiplet whereas in the aziridine (37) the corresponding aziridinyl protons had appeared as a singlet.

An attempted second ring-expansion on (38) with triethylamine hydrochloride paralleled the reaction of (25), giving the 2β-chloro-product (39). H-2 was



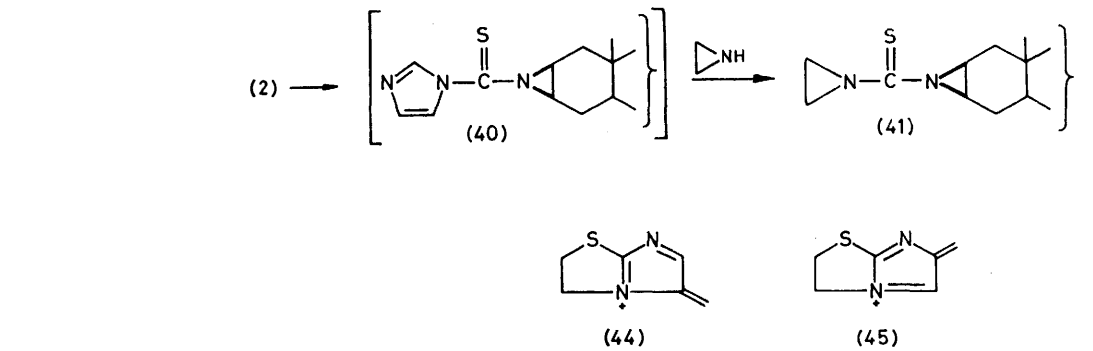
SCHEME 3

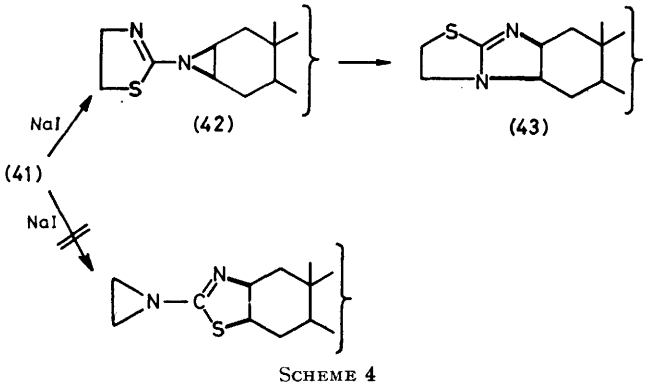
assigned equatorial stereochemistry ($W_{\frac{1}{2}}$ 7 Hz) but H-3 was obscured, and *trans*-diaxial stereochemistry for the C-2 and C-3 substituents can reasonably be assumed. Further cyclization of (39) was not observed.

A similar series of reactions was performed on the β-aziridine (2). The reaction with 1,1′-thiocarbonyldiimidazole occurred more rapidly, giving, according to t.l.c., an intermediate, probably of structure (40). It was also possible in this case to trap the intermediate with aziridine, giving the bis-aziridine (41) which showed a

coupling pattern for H-2 and H-3 typical of a 2β,3β-aziridine.

Again, ring-expansion of (41) could have given four possible products but, paralleling the α-series, sodium iodide–acetonitrile gave an aziridinyl thiazoline of structure (42) (Scheme 4). The mass spectrum of (42) showed the characteristic $M - 28$ ion,[12] and the n.m.r. spectrum showed 2β,3β-substitution.* Further treatment of (42) with either sodium iodide–acetonitrile or with triethylamine hydrochloride gave a common product (the former reaction being cleaner), shown to be the desired fused imidazo[2,1-*b*]thiazole derivative (43). In the n.m.r. spectrum the doublet (1 H) which had been observed in an extensive series of 2β,3β-fused heterocycles including oxazolines,[1] thiazolines, and aziridines was again observed (J 16 Hz). In the mass spectrum an abundant fragment ion at *m/e* 139 was assigned structure (44) or (45).





SCHEME 4

EXPERIMENTAL

General details are as previously reported.[1] High-resolution mass measurements of molecular ions were performed on samples which were homogeneous according to t.l.c. and n.m.r. spectroscopy.

Acetylation of 2β,3β-*Dihydro*-5α-*androst*-2-*eno*[2,3-b]-*azirin*-17-*one Ethylene Acetal* (1).—The steroid (1) (330 mg, 1.0 mmol) and acetic anhydride (1.3 ml) in pyridine (7 ml) were stirred at ambient temperature for 2 h. The mixture was poured into ice–water. The precipitated product was filtered off and dissolved in dichloromethane. This solution was washed with water, dried ($MgSO_4$), and the solvent removed *in vacuo* to yield 1′-*acetyl*-2β,3β-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one ethylene acetal* (3) (320 mg, 86%), m.p. 157—159 °C (from ether), $[\alpha]_D$ +4.5° (*c* 1.0), $\nu_{max.}$ (CH_2Cl_2) 1 685, 1 215, and 1 170 cm^{-1}, δ ($CDCl_3$) (0.75 and 0.81 (each 3 H, s, 13- and 10-Me), 2.08 (3 H, s, MeCO), 2.60 (2 H, m, 2β- and 3β-H), and 3.86 (4 H, s, 17-acetal) (Found: C, 74.0; H, 9.5; N, 3.5. $C_{23}H_{35}NO_3$ requires C, 73.95; H, 9.4; N, 3,75%).

Reaction of 1′-*Acetyl*-2β,3β-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one Ethylene Acetal* (3) *with Thiobenzoic* S-*Acid*.—To a solution of the steroid (3) (400 mg, 1.07 mmol) in benzene (20 ml) was added thiobenzoic *S*-acid (1 ml) and the mixture was set aside overnight at room temperature. The mixture was diluted with ether, then shaken with dilute sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and the solvent removed under reduced pressure to yield a dark red oil. Medium pressure column chromatography on silica gel, eluting with light petroleum–ethyl acetate, afforded first dibenzoyl disulphide (300 mg), m.p. 129—130 °C, identified from i.r. and n.m.r. spectral data. Further elution yielded 1′-benzoyl-2β,3β-dihydro-5α-androst-2-eno[2,3-*b*]azirin-17-one ethylene acetal (5) (242 mg, 52%), m.p. 188—190 °C, which proved identical to that obtained in a previous study.[1] The final product eluted was 3α-*acetamido*-2β-*mercapto*-5β-*androstan*-17-*one ethylene acetal* 2-*benzoate* (6) (180 mg, 33%), m.p. 142—145 °C (from dichloromethane–ether), $[\alpha]_D$ +22° (*c* 1.1), $\nu_{max.}$ (KBr) 3 300, 1 655, 1 528, 1 200, 1 168, 902, and 680 cm^{-1}, δ ($CDCl_3$) 0.84 and 0.99 (each 3 H, s, 13- and 10-Me), 2.01 (3 H, s, MeCO), 3.89 (4 H, s, 17-acetal), 4.13 (2 H, m, 2α- and 3β-H), 6.46 (1 H, d, J 7 Hz, NH), and 7.2—8.2 (5 H, m, Ph) (Found: M^+, 511.276 9. $C_{30}H_{41}NO_4S$ requires M, 511.275 7).

Treatment of (3) *with* 1 *Mol. Equiv. of Thiobenzoic* S-*Acid*.—The *N*-acetyl-α-aziridine (3) (747 mg, 2 mmol) in benzene (20 ml) was purged with nitrogen for 15 min and the mixture stirred overnight with thiobenzoic *S*-acid (280 mg, 2 mmol). Work-up as before and column chromatography on silica gel, eluting with light petroleum–ethyl acetate, afforded first the *N*-benzoyl-α-aziridine (5) (218 mg, corrected yield 38%), then the *N*-acetyl-α-aziridine (3) (254 mg), and the 3α-acetamido-2β-thiobenzoate (6) (153 mg, corrected yield 23%).

Attempted Reaction of 3α-*Acetamido*-2β-*mercapto*-5α-*androstan*-17-*one Ethylene Acetal* 2-*Benzoate* (6) *with Thio-*

* In 2β,3β-aziridines, including *N*-acyl examples,[1] a characteristic doublet (1 H, J 15 Hz) was observed, just outside the main steroid envelope.

benzoic S-Acid.—A mixture of the steroid (6) (15 mg, 0.03 mmol) and thiobenzoic *S*-acid (0.2 ml) in benzene was stirred at room temperature. After 20 h t.l.c. analysis indicated no trace of reaction.

Preparation of Acetic Benzoic Thioanhydride [3] (8).—Thiobenzoic *S*-acid (1.36 g, 0.98 mmol) was added to a stirred suspension of sodium hydride (300 mg, *ca.* 80% dispersion in oil) in benzene (35 ml). The mixture was stirred for 2 h and the precipitated solid was then filtered off, washed successively with benzene and light petroleum, and dried to yield *S*-sodium thiobenzoate (1.49 g, 94%) as a pale yellow solid. To a stirred suspension of dried, finely ground *S*-sodium thiobenzoate (1.49 g, 9.31 mmol) in dry ether (25 ml) at −15 °C, acetyl chloride (0.67 g, 8.53 mmol) in ether (15 ml) was added dropwise. The mixture was stirred at −15 °C for 4 h. This temperature was maintained and the precipitated sodium chloride was filtered off; light petroleum (10 ml) was added to the filtrate and any further salt which precipitated was filtered off. Repeating this with more light petroleum (25 ml) and setting the mixture aside at −15 °C for 1 h produced fine needles of acetic benzoic thioanhydride (8) (0.54 g, 32%), m.p. 16—20 °C (lit.,[3] 17—21 °C).

Reaction of 2β,3β-Dihydro-5α-androst-2-eno[2,3-b]*azirin-17-one Ethylene Acetal* (1) *with Acetic Benzoic Thioanhydride* (8).—The mixed thioanhydride (8) (18 mg, 0.1 mmol) was added to a solution of the steroid (1) (33 mg, 0.1 mmol) in benzene. T.l.c. analysis in several solvent systems showed the instantaneous formation of two products, the least polar having the same retention time as the *N*-benzoyl-α-aziridine (5) and the more polar, major product, the same retention time as the *N*-acetyl-α-aziridine (3). Chromatographic separation and spectroscopic comparison with authentic samples confirmed the structures.

Acetylation of 2α,3α-Dihydro-5α-androst-2-eno[2,3-b]*azirin-17-one Ethylene Acetal* (2).—Acetic anhydride (0.4 ml) was added to a solution of the steroid (2) (100 mg, 0.30 mmol) in pyridine (2 ml) and the mixture was stirred at room temperature for 2 h. Ice was added and on stirring the product precipitated. This precipitate was filtered off, dissolved in dichloromethane, and the solution was washed with water, and dried ($MgSO_4$). The solvent was evaporated off under reduced pressure to give *1′-acetyl-2α,3α-dihydro-5α-androst-2-eno*[2,3-b]*azirin-17-one ethylene acetal* (4) (89 mg, 79%), m.p. 183—185 °C (from methanol), $[\alpha]_D$ −9° (*c* 0.96), $\nu_{max.}$ 1 690, 1 290, 1 220, and 755 cm^{-1}, δ ($CDCl_3$), 0.83 and 0.85 (each 3 H, s, 13- and 10-Me), 2.08 (3 H, s, MeCO), 2.64 (2 H, m, 2α- and 3α-H), and 3.88 (4 H, s, 17-acetal) (Found: C, 73.7; H, 9.3; N, 3.7. $C_{23}H_{35}NO_3$ requires C, 73.95; H, 9.4; N, 3.75%).

Reaction of 1′-Acetyl-2α,3α-dihydro-5α-androst-2-eno[2,3-b]*azirin-17-one Ethylene Acetal* (4) *with Thiobenzoic S-Acid*.—Thiobenzoic *S*-acid (3 ml) was added to a solution of the steroid (4) (500 mg, 1.34 mmol) in benzene (25 ml) and the mixture was set aside for 2 days at room temperature. The solution was diluted with ether, washed with dilute sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and the solvents were removed *in vacuo* giving a dark red oil. Medium-pressure column chromatography on silica gel, eluting with light petroleum–ethyl acetate afforded first dibenzoyl disulphide (345 mg), m.p. 128—130 °C, which was identified from i.r. and n.m.r. spectral data. Further elution gave 1′-benzoyl-2α,3α-dihydro-5α-androst-2-eno[2,3-*b*]azirin-17-one ethylene acetal (9) (256 mg, 44%), m.p. 205—206 °C, which proved identical to that obtained in a previous study.[1] Continued elution yielded *2β-benzamido-3α-mercapto-5α-androstan-17-one ethylene acetal 3-benzoate* (10) (90 mg, 12%), m.p. 138—140 °C (from ether), $[\alpha]_D$ +48° (*c* 0.89), $\nu_{max.}$ 3 400, 1 660, 1 510, 1 200, 1 170, 900, and 680 cm^{-1}, δ ($CDCl_3$) 0.84 and 108 (each 3 H, s, 13- and 10-Me), 3.90 (4 H, s, 17-acetal) 4.46 and 4.20 (each 1 H, m, 2α- and 3β-H), 6.65 (1 H, d, *J* 7 Hz, NH), and 7.1—8.3 (10 H, m, Ph) (Found: M^+, 573.292 5. $C_{35}H_{43}NO_4S$ requires M, 573.291 3). The final product eluted was *2β-acetamido-3α-mercapto-5α-androstan-17-one ethylene acetal 3-benzoate* (11) (197 mg, 29%), m.p. 156—159 °C (from ether), $[\alpha]_D$ +41° (*c* 2.01), $\nu_{max.}$ (KBr) 3 580, 3 260, 1 650, 1 200, 1 012, and 685 cm^{-1}, δ ($CDCl_3$) 0.83 and 0.93 (each 3 H, s, 13- and 10-Me), 1.95 (3 H, s, MeCO–), 2.04 (s, OH exch.), 3.87 (4 H, s, 17-acetal), 4.05 (2 H, m, 2α- and 3β-H), 6.10 (1 H, d, *J* 7 Hz, NH), and 7.2—8.3 (5 H, m, Ph) (Found: M^+, 511.276 9. $C_{30}H_{41}NO_4S$ requires *M*, 511.275 7).

Reaction of 1′-Acetyl-2β,3β-dihydro-5α-androst-2-eno[2,3-b]*azirin-17-one Ethylene Acetal* (3) *with Thioacetic S-Acid*.—A solution of the steroid (3) (700 mg, 1.88 mmol) in toluene was purged with nitrogen, thioacetic *S*-acid (3 ml) added, and the mixture stirred overnight at room temperature. The mixture was diluted with ether and washed with dilute sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and the solvent removed *in vacuo*. Medium-pressure column chromatography on silica gel, eluting with light petroleum–ether afforded *3α-acetamido-2β-mercapto-5α-androstan-17-one ethylene acetal 2-acetate* (12) (570 mg, 68%), m.p. 132—134 °C (from ether—light petroleum), $[\alpha]_D$ +17° (*c* 0.83), $\nu_{max.}$ 3 280, 1 685, 1 640, 1 530, 1 165, 1 110, and 630 cm^{-1}, δ ($CDCl_3$) 0.85 and 0.92 (each 3 H, s, 13- and 10-Me), 1.99 (3 H, s, NHCO·*Me*), 2.31 (3 H, s, SCO·Me), 3.6—4.3 (6 H, m, 2α-H, 3β-H, and 17-acetal), and 6.06 (1 H, d, *J* 8 Hz, NH) (Found: M^+, 499.259 8. $C_{25}H_{39}NO_4S$ requires *M*, 499.260 0).

Reaction of 1′-Acetyl-2α,3α-dihydro-(5α-*androst-2-eno*[2,3-b]*azirin-17-one Ethylene Acetal* (4) *with Thioacetic S-Acid*.—A solution of the steroid (4) (400 mg, 1.07 mmol) in benzene was purged with nitrogen for 5 min. Thioacetic *S*-acid (3 ml) was added and the resultant mixture stirred at room temperature for 3 days. The reaction was diluted and washed with dilute sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and the solvent removed under reduced pressure. Medium-pressure column chromatography on silica gel, eluting with light petroleum–ethyl acetate, afforded *2β-acetamido-3α-mercapto-5α-androstan-17-one ethylene acetal 3-acetate* (13) (353 mg, 73%), m.p. 195—197 °C (from ether), $[\alpha]_D$ +27° (*c* 1.25), $\nu_{max.}$ (KBr) 3 300, 1 692, 1 650, 1 160, 1 105, and 945 cm^{-1}, δ ($CDCl_3$) 0.83 and 0.94 (each 3 H, s, 13- and 10-Me), 1.95 (3 H, s, NHCO·*Me*), 2.33 (3 H, s, SCO·Me), 3.5—4.3 (6 H, m, 2α-, 3β-H and 17-acetal), and 6.17 (1 H, d, *J* 8 Hz, NH) (Found: M^+, 449.256 2. $C_{25}H_{39}NO_4S$ requires *M*, 449.260 0).

Reaction of 3α-Amino-2β-chloro-5α-androstan-17-one (14) *with Carbon Disulphide*.—Carbon disulphide (5 ml) was added to a solution of the steroid (14) (290 mg, 0.90 mmol) in methanol (50 ml) and the resultant mixture brought to reflux. After gradual addition of sodium hydroxide solution (30 ml; 1M) the mixture was heated under reflux for a further 2 h. The excess of carbon disulphide was then distilled off, the mixture was cooled, and the fine crystals of product were filtered off. Recrystallisation from methanol afforded *2′-thioxo-2β,2′,3β,3′-tetrahydro-5α-androst-2-eno*[3,2-d]*thiazol-17-one* (15) (250 mg, 77%), m.p. 390 °C

(decomp.), $[\alpha]_D$ +208° (*c* 1.66), $\nu_{max.}$ (KBr) 3 240, 1 720, 1 480, and 1 023 cm^{-1}, δ (CD_3SOCD_3) 0.79 (6 H, s, 13- and 10-Me), 3.82br (1 H, m, 2β-H), 4.22 (1 H, m, sharp, 3β-H), and 10.07 (1 H, m, NH exch.) (Found: C, 66.0; H, 8.2; N, 4.0. $C_{20}H_{29}NOS_2$ requires C, 66.1; H, 8.0; N, 3.85%).

Methylation of *2′-Thioxo-2β,2′,3β,3′-tetrahydro-5α-androst-2-eno*[3,2-d]*thiazol-17-one* (15).—Sodium hydrogen carbonate (120 mg, 1.43 mmol) and methyl iodide (86 mg, 0.60 mmol) were added to a stirred solution of the steroid (15) (200 mg, 0.55 mmol) in acetone (30 ml) and the mixture was stirred at room temperature for 4 h. The mixture was added to water, the solid obtained was extracted into ether, and the etheral solution washed with water, dried ($MgSO_4$), and the solvent removed under reduced pressure. Column chromatography on silica gel, eluting with toluene–ether, afforded *2′-methylthio-2β,3β-dihydro-5α-androst-2-eno*[3,2-d]*thiazol-17-one* (16) (130 mg, 63%), m.p. 189—191 °C (from methanol), $[\alpha]_D$ +166° (*c* 0.62), $\nu_{max.}$ (KBr) 1 728, 1 550, 1 284, and 937 cm^{-1}, δ ($CDCl_3$) 0.84 (6 H, s, 13- and 10-Me), 2.54 (3 H, s, SMe), and 3.3—4.2 (2 H, m, 2β- and 3β-H) (Found: M^+, 377.184 8. $C_{21}H_{31}NOS_2$ requires *M*, 377.184 7).

Formation of 2′-Phenylimino-2β,2′,3β,3′-tetrahydro-5α-androst-2-eno[3,2-d]*thiazol-17-one Ethylene Acetal* (19).—To a solution of the α-aziridine (1) (330 mg, 1 mmol) in ether (50 ml), phenyl isothiocyanate (0.15 ml) in ether (20 ml) was added and the resultant mixture was left at room temperature for 4 h. The solution was then washed with water, dried ($MgSO_4$), and the solvent removed *in vacuo* to yield a foam (460 mg). Crystallization from dichloromethane–ether gave 1′-phenylthiocarbamoyl-2β,3β-dihydro-5α-androst-2-eno[2,3-*b*]azirin-17-one ethylene acetal (17) (320 mg, 69%), m.p. 199—201 °C, $[\alpha]_D$ +22° (*c* 0.73), $\nu_{max.}$ (KBr) 3 310, 1 595, 1 162, 750, and 685 cm^{-1}, δ ($CDCl_3$) 0.69 and 0.81 (each 3 H, s, 13- and 10-Me), 2.77 (2 H, m, 2β- and 3β-H), 3.90 (4 H, s, 17-acetal), 6.8-—7.6 (5 H, m, Ph), and 9.00 (1 H, m, NH exch.); *m/e* 466 (M^+), 331, 316, 303, 135, and 99.

The thiocarbamoyl-aziridine (17) (250 mg, 0.54 mmol), in acetone (30 ml) was refluxed with sodium iodide (1.1 g) for 4 h. The mixture was added to water, and the precipitated solid was filtered off, dissolved in dichloromethane, and the solution was washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to yield *2′-phenylimino-2β,2′,3β,3′-tetrahydro-5α-androst-2-eno*[3,2-d]*thiazol-17-one ethylene acetal* (19) (205 mg, 82%), m.p. 152—154 °C (from acetone–light petroleum), $[\alpha]_D$ −6.2° (*c* 1.29), $\lambda_{max.}$ 260 nm (log ε 4.07), $\nu_{max.}$ (KBr) 3 380, 1 635, 1 588, 1 160, 762, and 688 cm^{-1}, δ ($CDCl_3$) 0.74 and 0.81 (each 3 H, s, 13- and 10-Me), 3.45br (1 H, m, 2β-H), 3.89 (4 H, s, 17-acetal), 3.98 (1 H, m, sharp, 3β-H), and 6.8—7.7 (6 H, m, Ph and NH exch.) (Found: M^+, 466.266 2. $C_{28}H_{38}N_2O_2S$ requires *M*, 466.265 4).

Formation of 2′-Phenylimino-2α,2′,3α,3′-tetrahydro-5α-androst-2-eno[2,3-d]*thiazol-17-one Ethylene Acetal* (23).—To a solution of the β-aziridine (2) (290 mg, 0.88 mmol) in ether (50 ml) at 0 °C was added phenyl isothiocyanate (0.15 ml) in ether (20 ml) and the resultant mixture was left at room temperature for 4 h. The solution was then washed with water, dried ($MgSO_4$), and evaporated to yield 1′-phenylthiocarbamoyl-2α,3α-dihydro-5α-androst-2-enoazirin-17-one ethylene acetal (21) (320 mg, 78%), m.p. 185—189 °C (from ether–light petroleum), $[\alpha]_D$ +25° (*c* 1.1), $\nu_{max.}$ (KBr 3 160, 1 595, 1 170, 755, and 690 cm^{-1}, δ ($CDCl_3$) 0.79 and 0.83 (each 3 H, s, 13- and 10-Me), 2.80 (2 H, m, 2α- and 3α-H), 3.88 (4 H, s, 17-acetal), 6.7—7.6 (5 H, m, Ph), and 8.80 (1 H, m, NH exch.), *m/e* 466 (M^+), 331, 316, 303, 135, and 99.

A solution of the thiocarbamoyl-aziridine (21) (300 mg, 0.64 mmol) in acetone (40 ml) was refluxed with sodium iodide (1.4 g) for 2 h. The mixture was added to water, and the precipitated solid was filtered off and dissolved in dichloromethane, and the organic solution washed with water, dried ($MgSO_4$), and evaporated *in vacuo* to yield a white foam. Crystallisation from acetone gave *2′-phenylimino-2β,2′,3α,3′-tetrahydro-5α-androst-2-eno*[2,3-d]*thiazol-17-one ethylene acetal* (23) (255 mg, 85%), m.p. 228—231 °C, $[\alpha]_D$ −24° (*c* 1.56), $\lambda_{max.}$ 260 nm (log ε 4.09), $\nu_{max.}$ (KBr) 3 160, 1 635, 1 587, and 688 cm^{-1}, δ ($CDCl_3$) 0.80 and 0.93 (each 3 H, s, 13- and 10-Me), 3.33br (1 H, m, 3α-H), 3.87 (4 H, s, 17-acetal), 4.00 (1 H, m, sharp, 2α-H), and 6.8—7.6 (6 H, m, Ph and NH exch.) (Found: M^+, 466.264 7. $C_{28}H_{38}N_2O_2S$ requires *M*, 466.265 4).

Reaction of 2β,3β-Dihydro-5α-androst-2-eno[2,3-b]*azirin-17-one Ethylene Acetal* (1) *with 2-Chlorobenzothiazole and Triethylamine*.—A solution of the α-aziridine (1) (800 mg, 2.42 mmol) in xylene (30 ml) was refluxed with 2-chlorobenzothiazole (500 mg, 2.96 mmol) and triethylamine (3 ml) during 2 days. Further portions of triethylamine were added periodically. The mixture was diluted, washed with water, dried ($MgSO_4$), and the solvent removed. Column chromatography on silica gel, eluting with light petroleum–ethyl acetate, gave *1′-(benzothiazol-2-yl)-2β,3β-dihydro-5α-androst-2-eno*[2,3-b]*azirin-17-one ethylene acetal* (25) (725 mg, 65%), m.p. 248—249 °C (from ether), $[\alpha]_D$ +3.4° (*c* 1.19), $\lambda_{max.}$ 225, 267, and 196 nm (log ε 4.59, 4.32, and 4.11), $\nu_{max.}$ (KBr) 3 050, 1 590, 1 503, 1 435, 1 188, 748, and 715 cm^{-1}, δ ($CDCl_3$) 0.79 and 0.84 (each 3 H, s, 13- and 10-Me), 2.92 (2 H, m, 2β- and 3β-H), 3.86 (4 H, s, 17-acetal), and 7.1—7.9 (4 H, m, benzothiazole) (Found: C, 72.6; H, 7.8; N, 5.7; S, 6.4. $C_{28}H_{36}N_2O_2S$ requires C, 72.4; H, 7.8; N, 6.0; S, 6.9%).

Reaction of 1′-(Benzothiazol-2-yl)-2β,3β-dihydro-5α-androst-2-eno[2,3-b]*azirin-17-one Ethylene Acetal* (25) *with Triethylamine Hydrochloride*.—To a solution of the benzothiazolyl-aziridine (25) (200 mg, 0.43 mmol) in acetonitrile (20 ml) was added triethylamine hydrochloride (200 mg, 1.46 mmol) and the mixture was refluxed for 2 days. The mixture was added to water and the precipitated solid filtered off and dissolved in dichloromethane. The organic solution was washed with water and dried ($MgSO_4$), and the solvent removed *in vacuo*. Column chromatography on silica gel, eluting with toluene–ether, afforded *3α-(benzothiazol-2-yl)amino-2β-chloro-5α-androstan-17-one ethylene acetal* (27) (148 mg, 69%), m.p. 214—216 °C (from ether–light petroleum), $[\alpha]_D$ +49° (*c* 1.08), $\lambda_{max.}$ 227, 273, and 296 nm (log ε 4.76, 4.35, and 3.66), $\nu_{max.}$ (KBr) 3 355, 1 597, 1 540, 745, and 718 cm^{-1}, δ ($CDCl_3$; 100 MHz) 0.78 and 1.04 (each 3 H, s, 13- and 10-Me), 3.88 (4 H, s, 17-acetal), 4.00 (1 H, m, sharp, 3β-H), 4.46 (1 H, m, sharp, 2α-H), 6.86 (1 H, d, *J* 8 Hz, NH exch.), and 6.9—7.7 (4 H, m, benzothiazole) (Found: M^+, 500.222 0. $C_{28}H_{37}{}^{35}ClN_2O_2S$ requires *M*, 500.225 4).

Reaction of 2α,3α-Dihydro-5α-androst-2-eno[2,3-b]*azirin-17-one Ethylene Acetal* (2) *with 2-Chlorobenzothiazole and Triethylamine*.—A solution of the β-aziridine (2) (600 mg, 1.81 mmol) in xylene (40 ml) was refluxed with 2-chlorobenzothiazole (500 mg, 2.96 mmol) and triethylamine (2 ml) during 1 week. The mixture was diluted with xylene, washed with water, and dried ($MgSO_4$), and the solvent

removed *in vacuo*. Medium-pressure column chromatography on silica gel, eluting with light petroleum–ethyl acetate, afforded first 1′-(*benzothiazol*-2-*yl*)-2α,3α-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one ethylene acetal* (28) (360 mg, corrected yield 58%), m.p. 235—237 °C (from ether), $[\alpha]_D$ +2.6° (*c* 1.16), $\lambda_{max.}$ 225, 268, and 296 nm (log ε 4.69, 4.35, and 3.92), $\nu_{max.}$ (KBr) 3 030, 1 593, 1 512, 1 438, 1 195, 749, and 720 cm^{-1}, δ ($CDCl_3$; 100 MHz) 0.84 and 0.96 (each 3 H, s, 13- and 10-Me), 2.92 (2 H, m, 2α- and 3α-H), 3.88 (4 H, s, 17-acetal), and 7.0—7.8 (4 H, m, benzothiazole) (Found: C, 72.3; H, 5.8; S, 6.5. $C_{28}H_{36}N_2O_2S$ requires C, 72.4; H, 7.8; N, 6.0; S, 6.9%).

Further elution gave starting material (2) (157 mg).

Ring-expansion of 1′-(*Benzothiazol*-2-*yl*)-2α,3α-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one Ethylene Acetal* (28) *with Triethylamine Hydrochloride*.—Triethylamine hydrochloride (200 mg, 1.46 mmol) was added to a solution of the steroid (28) (230 mg, 0.495 mmol) in acetonitrile (30 ml) and the mixture was refluxed for 2 days. The mixture was poured into water and extracted with dichloromethane. The extracts were washed with water, dried ($MgSO_4$), and the solvent evaporated off. Column chromatography on silica gel afforded 2α,3α-*dihydro*-5α-*androst*-2-*eno*[2,3-b]-(*imidazo*[2,1-b]*benzothiazol*)-17-*one ethylene acetal* (30) (148 mg, 64%), m.p. 209—216 °C (decomp.), $[\alpha]_D$ −95° (*c* 0.43), $\lambda_{max.}$ 226, 267, and 302 nm (log ε 4.81, 4.25, and 3.91), $\nu_{max.}$ (KBr) 1 596, 1 580, 1 567, 1 460, 1 163, and 737 cm^{-1}, δ ($CDCl_3$, 100 MHz) 0.83 and 0.92 (each 3 H, s, 13- and 10-Me), 3.87 (4 H, s, 17-acetal), 4.0—4.6 (2 H, m, 2α- and 3α-H), and 6.6—7.4 (4 H, m, benzothiazole) (Found: M^+, 464.248 3. $C_{28}H_{36}N_2O_2S$ requires *M*, 464.249 7).

Formation of NN′-*Thiocarbonylbis*-(2α,3α-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirine*)-17,17′-*dione Bis*(*ethylene acetal*) (35).—A solution of 1,1′-thiocarbonyldi-imidazole (197 mg, 1.0 mmol; 90% tech. grade) in dichloromethane (10 ml) was added to a stirred solution of the α-aziridine (1) (330 mg, 1.0 mmol) in dichloromethane (10 ml). The resultant mixture was stirred at room temperature for a further 2 h and diluted with dichloromethane (30 ml). The resulting solution was washed with water and dried ($MgSO_4$), and the solvent evaporated off under reduced pressure to give a pale yellow solid. Repeated crystallisation from dichloromethane–ether afforded NN′-*thiocarbonylbis*-(2α,-3α-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirine*)-17,17′-*dione bis*-(*ethylene acetal*) (35) (220 mg, 62%), m.p. 221—227 °C (decomp.), $[\alpha]_D$ +7° (*c* 0.98), $\nu_{max.}$ (KBr) 1 398, 1 200, 1 160, 1 030, and 778 cm^{-1}, δ ($CDCl_3$) 0.77 and 0.83 (each 3 H, s, 13- and 10-Me), 2.80 (2 H, m, 2β- and 3β-H), and 3.85 (4 H, s, 17-acetal) (Found: M^+, 704.457 8. $C_{43}H_{64}N_2O_4S$ requires *M*, 704.458 7).

2β-(*Imidazol*-1-*yl*)-3α-*isothiocyanato*-5α-*androstan*-17-*one Ethylene Acetal* (36).—A cooled solution of the α-aziridine (1) (300 mg, 1 mmol) in dichloromethane (30 ml) was added dropwise, over 1 h, to a stirred solution of 1,1′-thiocarbonyldi-imidazole (400 mg, 2 mmol; 90% tech. grade) in dichloromethane (20 ml) at 0 °C. The mixture was stirred at ambient temperature for a further 2 h. The solution was concentrated to half volume under reduced pressure and chromatographed on neutral alumina, eluting with dichloromethane–methanol, to yield 2β-(*imidazol*-1-*yl*)-3α-*isothiocyanato*-5α-*androstan*-17-*one ethylene acetal* (36) (230 mg, (52%), m.p. 239—240 °C (from dichloromethane–ether), $[\alpha]_D$ +82° (*c* 0.68), $\nu_{max.}$ (KBr) 3 108, 2 012, 1 448, 1 223, 1 098, 897, 810, and 755 cm^{-1}, δ ($CDCl_3$) 0.63 and 0.81 (each 3 H, s, 10- and 13-Me), 3.87 (4 H, s, 17-acetal), 4.47 (2 H, m, 2α- and 3β-H), and 6.9—7.8 (3 H, m, imidazolyl-H) (Found: M^+, 441.244 4. $C_{25}H_{35}N_3O_2S$ requires *M*, 441.245 0).

Formation of 1′-(Δ²-*Thiazolin*-2-*yl*)-2β,3β,-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one Ethylene Acetal* (38).—A cooled solution of the α-aziridine (1) (400 mg, 1.21 mmol) in dichloromethane (30 ml) was added dropwise, over 35 min, to a stirred solution of 1,1′-thiocarbonyldi-imidazole (300 mg, 1.5 mmol; 90% tech. grade) in dichloromethane (20 ml) at 0 °C. The mixture was stirred for a further 15 min, when t.l.c. indicated the probable presence of 1′-[imidazol-1-yl(thiocarbonyl)]-2β,3β-dihydro-5α-androst-2-eno[2,3-*b*]-azirin-17-one ethylene acetal (34). To this solution was added aziridine (0.3 ml, 5.8 mmol) and the mixture was stirred at 0 °C for 20 min, washed with water, dried ($MgSO_4$), and the solvent removed *in vacuo* affording crude 1′-[aziridin-1-yl(thiocarbonyl)]-2β,3β,dihydro-5α-androst-2-eno[2,3-*b*]azirin-17-one ethylene acetal (37), $\nu_{max.}$ (KBr) 1 342, 1 295, 1 198, 1 133, 809, and 783 cm^{-1}, δ ($CDCl_3$) 0.77 and 0.82 (each 3 H, s, 13- and 10-Me), 2.53 (4 H, s, aziridinyl-H), 2.88 (2 H, m, 2β- and 3β-H), and 3.87 (4 H, s, 17-acetal). This crude product was dissolved in acetonitrile (80 ml), sodium iodide (1.6 g) was added and the mixture stirred at ambient temperature for 3 h. The mixture was added to water and the precipitated solid filtered off, dissolved in dichloromethane, washed with water, dried ($MgSO_4$), and the solvent evaporated off to yield a pale yellow foam. Medium-pressure column chromatography on silica gel, eluting with light petroleum–ethyl acetate, gave 1′-(Δ²-*thiazolin*-2-*yl*)-2β,3β-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one ethylene acetal* (38) (330 mg, 66%), m.p. 195—196 °C (from ether–light petroleum), $[\alpha]_D$ +3° (*c* 1.07), $\lambda_{max.}$ 210 nm (log ε 4.25), $\nu_{max.}$ (KBr) 1 605, 1 307, 1 158, 1 011, 940, and 796 cm^{-1}, δ ($CDCl_3$) 0.74 and 0.81 (each 3 H, s, 13- and 10-Me), 2.60 (2 H, m, 2β- and 3β-H), and 3.1—4.4 (8 H, m, 17-acetal and thiazoline) (Found: M^+, 416.251 9. $C_{24}H_{36}N_2O_2S$ requires *M*, 416.249 7).

Reaction of 1′-(Δ²-*Thiazolin*-2-*yl*)-2β,3β,*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one Ethylene Acetal* (38) *with Triethylamine Hydrochloride*.—Triethylamine hydrochloride (100 mg, 0.73 mmol) was added to a solution of the steroid (38) (100 mg, 0.24 mmol) in acetonitrile (4 ml) and the solution was refluxed for 2.5 h. The mixture was added to water, the resulting suspension extracted with ether, the ethereal solution washed with water and dried ($MgSO_4$), and the solvent removed *in vacuo* to yield an off-white solid (85 mg). Slaking with ether and crystallization from dichloromethane–ether gave 2β-*chloro*-3α-(Δ²-*thiazolin*-2-*yl*)*amino*-5α-*androstan*-17-*one ethylene acetal* (39) (62 mg, 57%), m.p. 206—210 °C, $[\alpha]_D$ +44° (*c* 1.0), $\lambda_{max.}$ 214 and 225 nm (log ε 4.42 and 4.34), $\nu_{max.}$ (KBr) 3 195, 1 610, 1 595, 1 535, 1 160, and 1 030 cm^{-1}, δ ($CDCl_3$) 0.83 and 1.09 (each 3 H, s, 13- and 10-Me), 3.1—4.2 (9 H, m, 17-acetal, 3β- and thiazoline), and 4.45 (2 H, m, 2α-H and NH exch.) (Found: M^+, 452.227 1. $C_{24}H_{37}{}^{35}ClN_2O_2S$ requires *M*, 452.226 4).

Formation of 1′-(Δ²-*Thiazolin*-2-*yl*)-2α,3α-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one Ethylene Acetal* (42).—A cooled solution of the β-aziridine (2) (300 mg, 0.91 mmol) in dichloromethane (30 ml) was added dropwise, over 10 min, to a stirred solution of 1,1′-thiocarbonyldi-imidazole (300 mg, 1.5 mmol; 90% tech. grade) in dichloromethane (40 ml) at −23 °C. The mixture was stirred for a further 5 min, and from t.l.c. evidence it appeared that 1′-[imidazol-1-yl-(thiocarbonyl)]-2α,3α-dihydro-5α-androst-2-eno[2,3-*b*]-azirin-17-one ethylene acetal (40) had been formed. Aziri-

dine (0.3 ml, 5.8 mmol) was added and the mixture was stirred at −23 °C for 30 min, washed with water, dried ($MgSO_4$), and the solvent evaporated off under reduced pressure giving crude 1′-[*aziridin*-1-*yl*(*thiocarbonyl*)]-2α,3α-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one ethylene acetal* (41). Purification by washing with ether gave pure (41) (310 mg), m.p. 180—185 °C, $[\alpha]_D$ −10° (*c* 0.57), $\nu_{max.}$ (KBr) 1 375, 1 292, 1 206, 1 159, 795, and 786 cm^{-1}, δ ($CDCl_3$) 0.83 (6 H, s, 13- and 10-Me), 2.48 (4 H, s, aziridine), 2.90 (2 H, m, 2α- and 3α-H), and 3.87 (4 H, s, 17-acetal) (Found: M^+, 416.251 3. $C_{24}H_{36}N_2O_2S$ requires *M*, 416.249 7).

The crude product was dissolved in acetonitrile (50 ml), sodium iodide (1.6 g) added, and the mixture stirred at ambient temperature for 5 h. The mixture was added to water and the precipitate which formed was filtered off. This solid was dissolved in dichloromethane and the organic solution washed with water, dried ($MgSO_4$), and the solvent removed *in vacuo* to give a yellow solid. Medium-pressure column chromatography on silica gel, eluting with light petroleum–ethyl acetate, afforded 1′-(Δ²-*thiazolin*-2-*yl*)-2α,3α-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one ethylene acetal* (42) (210 mg, 56%), m.p. 177—179 °C (from methanol), $[\alpha]_D$ +2° (*c* 0.51), $\lambda_{max.}$ 212 nm (log ε 4.02), $\nu_{max.}$ (KBr) 1 605, 1 405, 1 302, 1 162, 1 005, and 742 cm^{-1}, δ ($CDCl_3$) 0.80 and 0.85 (each 3 H, s, 13- and 10-Me), 2.60 (2 H, m, 2α- and 3α-H), and 3.0—4.2 (8 H, m, 17-acetal and thiazoline) (Found: M^+, 416,248 8. $C_{24}H_{36}N_2O_2S$ requires *M*, 416.249 7).

Reaction of 1′-(Δ²-*Thiazolin*-2-yl)-2α,3α-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one Ethylene Acetal* (42) *with Sodium Iodide*.—The steroid (42) (100 mg, 0.24 mmol) and sodium iodide (300 mg) were refluxed in acetone for 9 h. The mixture was allowed to cool and then added to water to give a white precipitate. The solid was filtered off, dissolved in dichloromethane, and the organic solution was washed with water, dried ($MgSO_4$), and the solvent removed *in vacuo* to yield 2α,2′,3α,3′-*tetrahydro*-5α-*androst*-2-*eno*-[3,2-e](*imidazo*[2,1-b]*thiazol*)-17-*one ethylene acetal* (43) (73 mg, 73%), m.p. 220—225 °C, $[\alpha]_D$ −4° (*c* 1.0), $\lambda_{max.}$ 277 nm (log ε 3.22), $\nu_{max.}$ (KBr) 1 585, 1 163, and 1 025 cm^{-1}, δ ($CDCl_3$; 100 MHz) 0.84 and 0.92 (each 3 H, s, 13- and 10-Me), and 3.1—4.5 (10 H, overlapping m, 2α-, 3α-, thiazolidine, and 17-acetal) (Found: M^+, 416.248 7. $C_{24}H_{36}N_2O_2S$ requires *M*, 416.249 7).

Reaction of 1′-(Δ²-*Thiazolin*-2-*yl*)-2α,3α-*dihydro*-5α-*androst*-2-*eno*[2,3-b]*azirin*-17-*one Ethylene Acetal* (42) *with Triethylamine Hydrochloride*.—The steroid (42) (80 mg, 0.19 mmol) and trimethylamine hydrochloride (80 mg, 0.58 mmol) in acetonitrile were refluxed for 9 h. The mixture was poured into water and extracted with ether. The ethanol solution was washed with water, dried ($MgSO_4$), and the solvent removed under reduced pressure to yield a white solid. Crystallisation from dichloromethane–ether gave 2α,2′,3α,3′-tetrahydro-5α-androst-2-eno[3,2-*e*](imidazo-[2,1-*b*]thiazol)-17-one ethylene acetal (43) (47 mg, 59%), which proved identical in all respects to that prepared previously.

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