Synthetic Studies Relevant to Biosynthetic Research on Vitamin B_{12}. Part 11.[1] Modification of the East and West Building Blocks and Study of Different Assembly Methods for Synthesis of Isobacteriochlorins

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The eastern and western building blocks required for the photochemical route to isobacteriochlorins have been synthesized by a C–C bond-forming step which leaves a cyano group on the bridge carbon, *e.g.* **5**. Two methods have been developed to remove this cyano residue which use retro-Mannich reactions to eliminate either an aminomethyl group, resulting from reduction of the nitrile, or the corresponding sulfonamido group. Two effective ways to carry out the final steps of the isobacteriochlorin synthesis have also been developed.

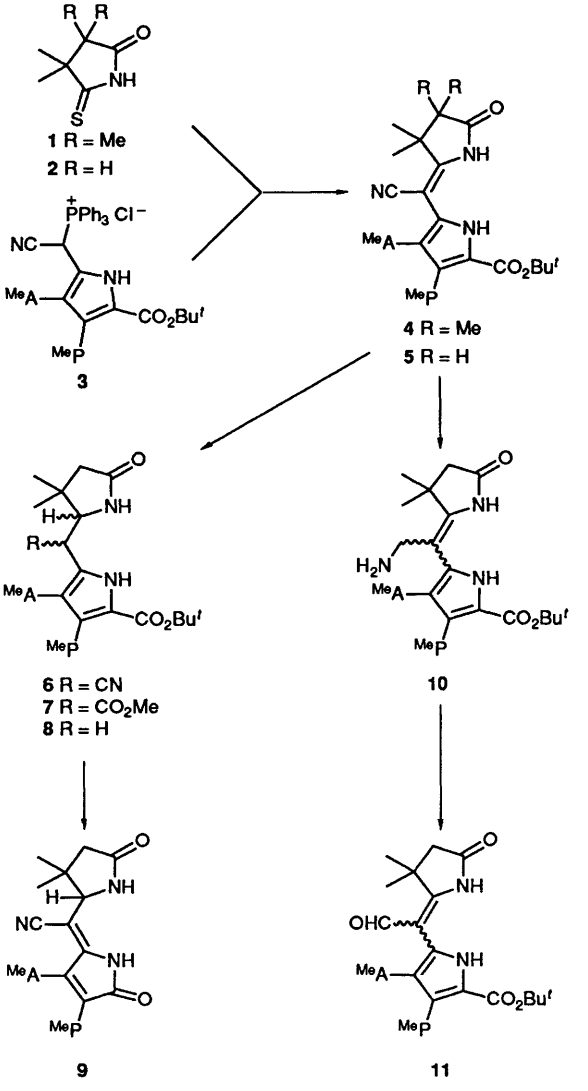
The experiments described in Part 10[1] led to the development of a highly effective method for linking of the pyrrolic rings of southern building blocks to the reduced rings of northern building blocks for synthesis of the isobacteriochlorin macrocycle. This involved the base-catalysed coupling of a Wittig salt, *e.g.* **3**, with a monothioimide, *e.g.* **1**, to form the product **4** and this method was used[2] subsequently to prepare the dimethylated system **5** from the precursors **2** and **3**. The cyano function was essential for the success of this strategy, so it was necessary to solve the problem of removing it once its task was completed. In principle, this might be achieved by manipulating compounds derived from the initial product **5**. Alternatively, since we knew that the cyano function can be carried through the entire synthesis,[2] its removal after completion of the isobacteriochlorin macrocycle could also be considered. Examination of both options is described in this paper.

Results and Discussion

Initial Experiments on Removal of the Cyano Group.—The model system **5** was used for most of these experiments. The first approach aimed at reduction of the α,β-unsaturated nitrile and though the methods commonly expected to achieve this reduction failed, that based on dissolving magnesium in methanol[3] yielded the separable diastereoisomers **6** in >80% yield. Although cyanide ion is a poor leaving group, it was hoped that electron release, *e.g.* from the pyrrole anion, would assist its expulsion. In the event, none of the conditions tried led to this elimination, nor did attempted enhancement of the leaving qualities of the cyano function, *e.g.* by complexation with cobalt(II) ions.[4]

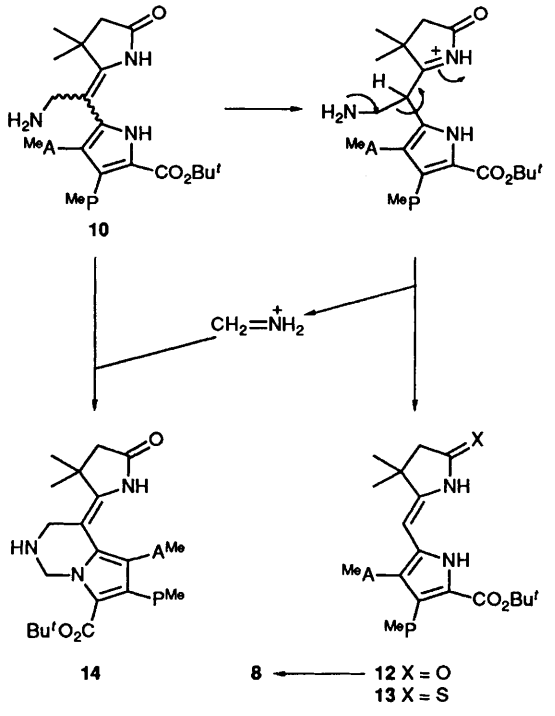
Attention therefore turned to oxidation of the methine centre carrying the cyano group, but the mixture of nitriles **6** was surprisingly resistant to several different oxidizing conditions and, for example, was recovered unchanged after heating for 24 h in boiling acetic acid with lead tetraacetate. Cerium(IV) ammonium nitrate did achieve oxidation but the product, in 71% yield, was the bis-lactam **9** (see Scheme 1).

A promising lead came from the observation that a by-product from the magnesium–methanol reduction of the nitrile **5** was the ester **7** formed in ~10% yield as a single diastereoisomer. This is clearly formed by methanolysis of the saturated system **6** since the unsaturated nitrile **5** was unaffected by being heated in methanol with magnesium methoxide. Support came from the fact that, under these conditions, the saturated system **6** gave 7% of the ester and also 9.5% of this ester by treatment with magnesium in methanol. However, these low yields could not be improved, probably because the initial product of base-catalysed methanolysis is the imidate and the equilibrium lies heavily towards the nitrile.



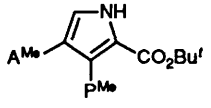
Scheme 1 $A^{Me} = CH_2CO_2Me$, $P^{Me} = CH_2CH_2CO_2Me$

Our efforts then turned towards the aminomethyl derivative **10** which could be prepared in high yield as a mixture of stereoisomers by reduction of the nitrile **5** over Raney nickel.[2] It



Scheme 2

Table 1 Survey of trapping agents for retro-Mannich reaction

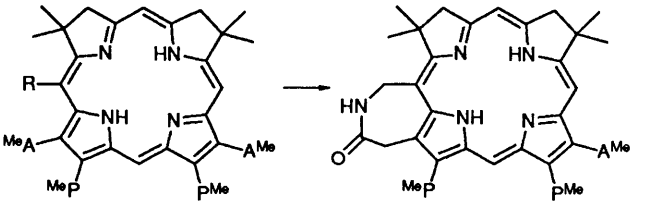
Trapping agent	Solvent	Temp. (T/°C)	Yield of **12** (%)
Imidazole	Toluene	110	11
	Anisole	90	28
1,2-Dihydroxybenzene	Anisole	90	36
1,3-Diaminopropane	Anisole	90	41
1,2-Diaminobenzene	Anisole	90	~60
Propane-1,3-dithiol	Anisole	90	65

was envisaged that conversion of the aminomethyl group into a formyl residue, followed by oxidation to the corresponding carboxylic acid, would allow its removal by decarboxylation. Accordingly, the amines were treated with a 4-formyl-*N*-methylpyridinium salt.[5] The aldehyde **11** was produced in 40% yield with 34% of the starting material being recovered. Surprisingly, the aldehyde was resistant to oxidation and experiments with nine different oxidizing agents either had no effect or, in two cases, led to serious degradation.

Fortunately at this stage, a clue which led to the successful approach came from other studies. The key observation[2] was that palladium-catalysed transfer hydrogenation from menthene to the nitrile **5** gave, among other products, the saturated lactam **8** in up to 40% yield. Scheme 2 shows the most probable sequence by which this product could be formed, involving fragmentation of the amine by a retro-Mannich reaction followed by further reduction. Clearly, if conditions could be established for a smooth retro-Mannich step, then the nitrile problem would be solved.

It was quickly observed that when solutions of the aminomethyl system **10** were prepared in dichloromethane for experiments on the retro-Mannich reaction, the material in solution spontaneously fragmented to yield the desired lactam **12**. At partial conversion, a 20% yield of the lactam **12** was accompanied by 34% recovery of starting material and other products, one of which had a relative molecular mass 12 mass units higher than that of the starting material **10**. This increase in mass, and the NMR spectrum of the product, suggested that it had arisen by reaction of the starting amine **10** with the retro-Mannich fragment $CH_2{=}\overset{+}{N}H_2$. The structure **14** fitted the data well but has not been established as there are other obvious ways to introduce a methylene group to afford isomeric cyclic systems. However, the important conclusion was that the yield of desired product **12** should be improved by trapping of the retro-Mannich fragment with some external reagent. The results of a survey of a range of possible trapping agents are collected in Table 1 and they show that this approch raised the yields of the desired product **12** to preparative levels. One good solution to the nitrile problem was thus available.

At this stage, it was decided to investigate whether removal of the cyano group could be delayed until after formation of the isobacteriochlorin. The material used for these experiments was the 10-cyanoisobacteriochlorin[2] **15**, kindly provided by Dr. D. M. Arnott. Attempted hydrogenation of the nitrile catalysed by Raney nickel as in the previous section resulted in rapid reduction of the macrocycle. This difficulty was overcome by conversion of the isobacteriochlorin **15** into its zinc(II) complex, which could then be hydrogenated without attack on the main chromophore. However, acid-catalysed demetallation of the reduction product afforded not the required amine **16** but the seven-membered lactam **18** and this was always the product under a variety of conditions tested for the reduction (Scheme 3). Attempted trapping of the amine by carrying out the

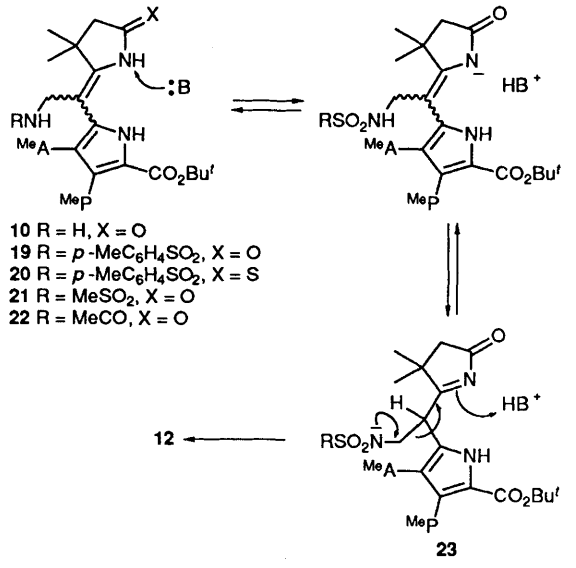


Scheme 3

hydrogenation in a 5:1 mixture of trifluoroacetic acid (TFA) and its anhydride (TFAA) gave, after demetallation, 90% of recovered starting material **15**, the only other product being the isobacteriochlorin **17** lacking the cyano function (3–5%). It was this result which first indicated that protection of the primary amine with a strongly electron-withdrawing group might be a promising approach, and the first studies were carried out by using the amines **10** as shown in Scheme 4.

Use of Sulfonylated Amines in the Retro-Mannich Reaction.— The mixture of *E*- and *Z* amines **10** was converted into the corresponding mixture of toluene-*p*-sulfonamides **19**. The major isomer (3 parts) could be crystallized and so separated from the amorphous minor isomer (2 parts). When the mixture was heated in anisole with *N,N'*-dimethylethylenediamine (found by now to be an even better trapping agent than those in Table 1), the desired lactam was obtained solely as the *Z*-isomer **12** in 80% yield. The retro-Mannich reaction worked equally well with the mixture of methanesulfonamides **21**; again only the *Z*-isomer **12** was obtained, in 73% yield.

The *E* and *Z* acetamides **22** were also prepared but they did not undergo the retro-Mannich reaction under any of the conditions used above. It seems probable that the acidity of the sulfonamide group is important in this chemistry; if the

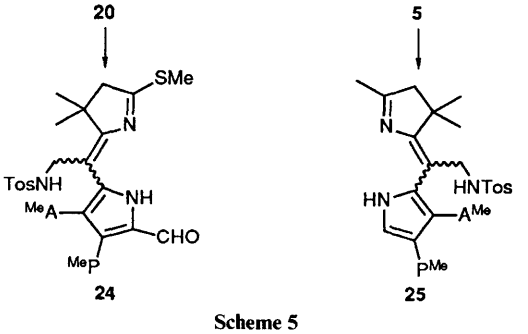


Scheme 4

equilibria shown in Scheme 4 led to formation of even a small amount of the key intermediate **23**, then fragmentation and trapping of the retro-Mannich product would pull the equilibria over to the desired material **12**.

The development of the retro-Mannich reaction based on sulfonamides proved to be very important for the synthesis of sirohydrochlorin octamethyl ester to be described in Part 12.[6]

It was hoped that similar chemistry might also be successful after the isobacteriochlorin macrocycle had been constructed from the west **24** and east **25** building blocks (see Scheme 5). As

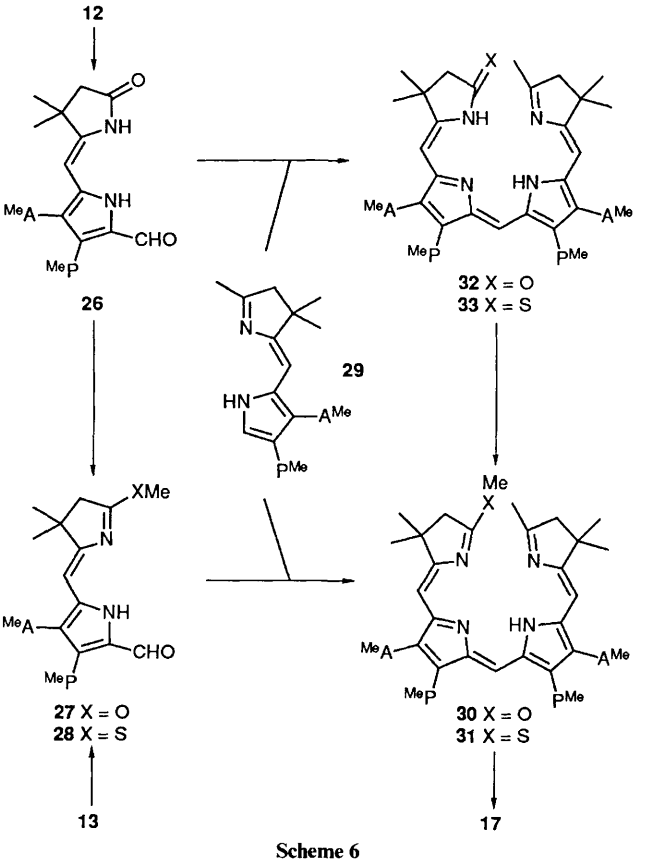


Scheme 5

it turned out, these studies could not be made because the required isobacteriochlorin could not be built in this way; only brief comment is made here on the work. This result is now not surprising since recent studies[7,8] have shown that substitution at the bridge position of even one of the building blocks such as **24** strongly affects the chemistry; in the failed route, both halves, **24** and **25**, carried bulky bridge substituents. However, the intermediates **19**, **20** and **24** were fully characterized and are described in the Experimental section.

The outcome of all the work so far described was to provide very effective methods for removal of the cyano group based on retro-Mannich reactions involving either the derived aminomethyl or toluene-*p*-sulfonamidomethyl derivatives. It was also clear that the cyano group should be removed before attempts to form the isobacteriochlorin macrocycle are begun.

Some Modifications of the Photochemical Synthesis of Isobacteriochlorins.—The photochemical synthesis of isobacteriochlorin **17** was one of the first to be described[9] and the 18π-electron system required for the photochemical cyclization was generated by formation of an imidate **30**, *i.e.* in the oxygen series **12** → **26** → **27** + **29** → **30** → **17**. An alternative was



Scheme 6

provided by the present studies when it was shown that, by working in the sulfur series, an equally effective synthesis of the isobacteriochlorin **17** could be achieved by the series **13** → **28** + **29** → **31** → **17**. Advantage was gained from the higher stability of the thioimidate system.

This experience led us to study a third way to use the building blocks for isobacteriochlorin synthesis. When the formyl lactam[9] **26** was condensed with the α-free pyrrole[9] **29**, the crystalline seco-lactam **32** was isolated in 65% yield. Treatment of this lactam with Lawesson's reagent afforded the seco-thiolactam **33** in 94% yield as a stable, readily handled material. Trimethyl orthoformate and TFA then converted this product into the seco-thioimidate **31**, which was cyclized photochemically to give the isobacteriochlorin **17** in 82% yield (Scheme 6).

The crystals of the seco-lactam **32** prepared above were suitable for structure determination by X-ray analysis and Fig. 1 shows the helical conformation of the molecule. The two carbons which become bonded together in the photochemical cyclization of the imidate **30** or thioimidate **31** lie only 3.52 Å apart in the lactam **32**, this distance being slightly over the sum of the two van der Waals' radii. In addition, the conformation in solution of a related seco-lactam **34** was studied by NMR spectroscopy; this material was available from the corresponding imidate (see preceding paper[1]) as a result of adventitious hydrolysis during studies of its cyclization. NMR difference spectroscopy showed clear nuclear Overhauser enhancements (NOEs) between protons on opposite ends of the molecule as indicated on structure **34**. This further supports the illustrated helical conformation. Finally, the ^{1}H NMR spectrum of the previous seco-lactam **32** at −95 °C showed that the two *C*-methyl groups on ring A and also those on ring D were no longer equivalent. A slow change (on the NMR time-scale) of one helical conformation into the other at low temperature could account for this observation which, however, does not by itself demonstrate helicity.

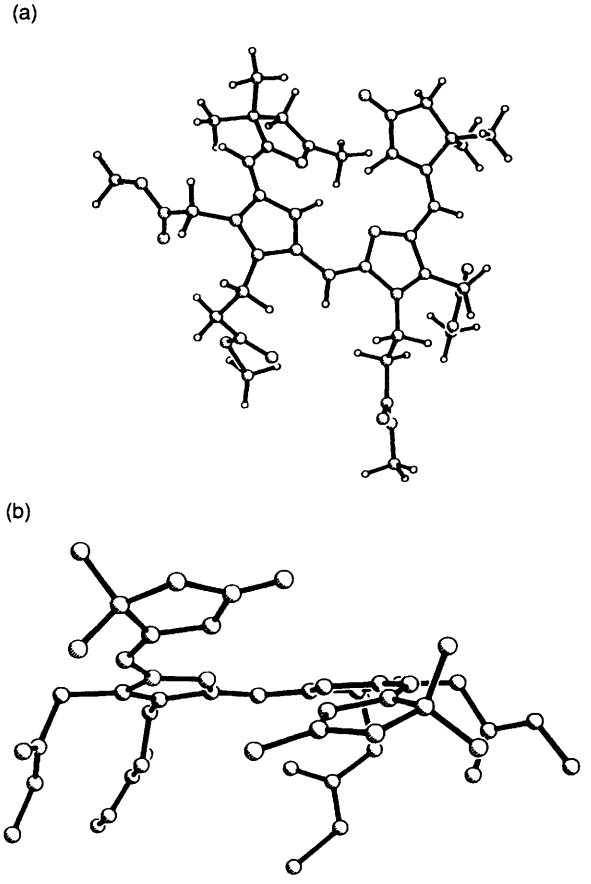
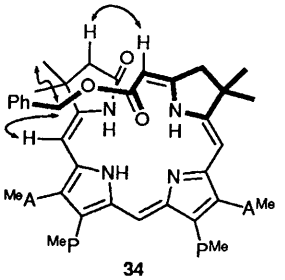


Fig. 1 Structure of seco-lactam **32** determined by X-ray analysis viewed from (a) above and (b) the side of the molecule.



34

The various advances in methodology here described, together with those in the preceding paper,[1] provided the firm foundation for a logical attack on the synthesis of the octamethyl ester of the natural dimethylated isobacteriochlorin, sirohydrochlorin, which has been reported briefly;[10] the full paper is in preparation.[6] In addition, the successful use of these methods for the synthesis of the monomethylated chlorin, Faktor-I octamethyl ester, has already been fully described.[11]

Experimental

General directions are as in the preceding paper.[1]

tert-*Butyl* 5-*Cyano*-8-(2-*methoxycarbonylethyl*)-7-*methoxycarbonylmethyl*-3,3-*dimethyl*-1-*oxo*-1,2,3,4,5,10-*hexahydrodipyrrin*-9-*carboxylate* **6** *and its* 5-*Methoxycarbonyl Analogue* **7** [*With Dr P. J. Harrison and Dr Z.-C. Sheng*].—To a solution of nitrile **5** (1.0 g) in dry methanol (30 cm^3) were added magnesium turnings (2.5 g). The mixture was stirred rapidly until the reaction started and was then cooled in an ice-bath when the reflux became too vigorous. After 4 h further dry methanol (10 cm^3) was added. After the magnesium had entirely dissolved, the mixture was cooled, poured onto 2 mol dm^{-3} hydrochloric acid (200 cm^3)–ice (100 g), and extracted with dichloromethane (200 cm^3, then 2 × 100 cm^3) and the extracts were dried and evaporated. Flash chromatography [eluent, methyl acetate–hexane (7:3)] gave recovered starting material (303 mg, 30%), *saturated nitrile* **6** (450 mg, 45%) as a mixture of diastereoisomers, and the *saturated ester* **7** (103 mg, 10%) (Found: M^+, 508.2422. $C_{25}H_{36}N_2O_9$ requires *M*, 508.2421); λ_{max}/nm 273; ν_{max}/cm^{-1} 3475, 2952, 1735, 1698, 1430 and 1365; δ_H (C; CD_2Cl_2) 0.86 and 0.94 (each 3 H, s, Me), 1.54 (9 H, s, Bu^t), 2.10 and 2.12 (each 1 H, ABq, *J* 16, CH_2CONH), 2.52 (2 H, t, *J* 8, $CH_2CH_2CO_2$), 2.92 (2 H, t, *J* 8, $CH_2CH_2CO_2$), 3.47 and 3.58 (each 1 H, d, *J* 17, CH_2CO_2), 3.64, 3.67 and 3.69 (each 3 H, s, OMe), 3.84 and 3.91 (each 1 H, d, *J* 10, CHCHN) and 5.91 and 9.12 (each 1 H, br s, NH).

The diastereoisomers of the nitrile **6** could be separated by PLC (developer, 5% methanol in dichloromethane). The higher R_f isomer was obtained as an *oil* (Found: M^+, 475.2304. $C_{24}H_{33}N_3O_7$ requires *M*, 475.2318); δ_H (E; CD_2Cl_2) 1.33 (6 H, s, 2 × Me), 1.41 (9 H, s, Bu^t), 2.09 and 2.47 (each 1 H, ABq, *J* 17, CH_2CONH), 2.45 (2 H, m, $CH_2CH_2CO_2$), 2.65 and 2.95 (each 1 H, m, $CH_2CH_2CO_2$), 3.59 and 3.77 (each 1 H, d, *J* 15, CH_2CO_2), 3.62 and 3.68 (each 3 H, s, OMe), 3.76 and 4.06 (each 1 H, d, *J* 12, CHCHN) and 7.15 and 11.6 (each 1 H, br s, NH). The lower R_f isomer was also obtained as an *oil* (Found: M^+, 475.2319); δ_H (E; CD_2Cl_2) 1.18 and 1.35 (each 3 H, s, Me), 1.52 (9 H, s, Bu^t), 2.09 and 2.64 (each 1 H, ABq, *J* 17, CH_2CONH), 2.49 (2 H, m, $CH_2CH_2CO_2$), 2.93 (2 H, t, *J* 8, $CH_2CH_2CO_2$), 3.48 and 3.63 (each 1 H, d, *J* 17, CH_2CO_2), 3.55 (1 H, br s, CHCHN) 3.63 and 3.68 (each 3 H, s, OMe), 4.06 (1 H, d, *J* 3, CHCHN) and 7.45 and 10.3 (each 1 H, br s, NH).

5-*Cyano*-2-(2-*methoxycarbonylethyl*)-3-*methoxycarbonylmethyl*-7,7-*dimethyl*-6,7-*dihydrodipyrrin*-1,9(8H,10H)-*dione* **9**.—To a stirred solution of the nitrile **6** (27 mg) and sodium acetate (18.7 mg) in acetic acid (3.3 cm^3) was added a solution cerium(IV) ammonium nitrate (12.5 mg) in water (0.2 cm^3). After 10 min dichloromethane (15 cm^3) was added, the mixture was washed with 10% aq. sodium hydrogen carbonate until the aqueous layer remained basic, and the organic layer was then dried and evaporated. PLC gave the *bis-lactam* **9** (15.8 mg, 71.5%) (Found: M^+, 389.1589. $C_{19}H_{23}N_3O_6$ requires *M*, 389.1587); λ_{max}/nm 260 and 352; ν_{max}/cm^{-1} 3450, 1740, 1690 and 1425; δ_H (C; CD_2Cl_2) 1.14 and 1.34 (each 3 H, s, Me), 2.10 and 2.51 (each 1 H, d, *J* 17, CH_2CONH), 2.60 (4 H, m, $CH_2CH_2CO_2$), 3.61 and 3.73 (each 3 H, s, OMe), 3.94 (2 H, s, CH_2CO_2), 4.34 (1 H, d, CHNH) and 6.83 and 9.32 (each 1 H, br s, NH).

tert-*Butyl* 5-*Formyl*-8-(2-*methoxycarbonylethyl*)-7-*methoxycarbonylmethyl*-3,3-*dimethyl*-1-*oxo*-1,2,3,10-*tetrahydrodipyrrin*-9-*carboxylate* **11**.—A solution of freshly prepared amine[2] **10** (81 mg) in dichloromethane (2.1 cm^3)–*N*,*N*-dimethylformamide (0.66 cm^3) was stirred with *N*-methylpyridinium-4-carbaldehyde phenylsulfonate (67 mg). After 2 h, triethylamine (56 mm^3) was added followed, after a further 30 min, by saturated aq. oxalic acid (2 cm^3). After 2 h the mixture was partitioned between dichloromethane (30 cm^3) and water (30 cm^3), the aqueous layer was extracted with dichloromethane (3 × 15 cm^3), and the combined organic layers were dried and evaporated. PLC [developer, methyl acetate–hexane (9:1)] gave a mixture of (E)-and (Z)-*aldehydes* **11** (32.3 mg, 40%) (Found: M^+, 476.2157. $C_{24}H_{32}N_2O_8$ requires *M*, 476.2159); λ_{max}/nm 272 and 325sh; ν_{max}/cm^{-1} 3498, 3248, 2990, 1740, 1668 and 1550; δ_H (C; CD_2Cl_2) (major isomer) 1.03 and 1.14 (each 3 H, br s, Me), 1.55 (9 H, s, Bu^t), 2.35 (2 H, s, CH_2CONH), 2.57 (2 H, br t, *J* 8, $CH_2CH_2CO_2$), 2.97 (2 H, t, *J* 8,

$CH_2CH_2CO_2$), 3.32 and 3.49 (each 1 H, br d, CH_2CO_2), 3.61 and 3.62 (each 3 H, s, OMe), 9.13 (1 H, s, CHO) and 9.61 and 11.46 (each 1 H, br s, NH). An observed NOE between the aldehydic proton and the lactam NH suggested that this major isomer has the *Z* configuration. A small amount (~10%) of the opposite isomer was evidenced by peaks at δ_H 3.65 and 3.67 (OMe) and 10.08 (CHO).

tert-*Butyl* 8-(2-*Methoxycarbonylethyl*)-7-*methoxycarbonylmethyl*-3,3-*dimethyl*-1-*oxo*-1,2,3,10-*tetrahydrodipyrrin*-9-*carboxylate* **12**.—Freshly prepared amine[2] **10** (13.2 mg) was dried under high vacuum and dissolved in anisole (2 cm^3) under argon. Propane-1,3-dithiol (28 mm^3) was added and the mixture was heated to 90 °C for 5.5 h and then evaporated under high vacuum. PLC [developer, dichloromethane–methanol (9:1)] gave the *meso*-free lactam **12** (8.1 mg, 65%), identical by FD-MS, NMR and TLC with authentic material.[9]

tert-*Butyl* (E)- *and* (Z)-8-(2-*Methoxycarbonylethyl*)-7-*methoxycarbonylmethyl*-3,3-*dimethyl*-1-*oxo*-5-(p-*tolylsulfonylaminomethyl*)-1,2,3,10-*tetrahydropyrrin*-9-*carboxylate* **19**.—Freshly prepared amine[2] **10** (115 mg) was stirred under argon in pyridine (5 cm^3) with toluene-*p*-sulfonyl chloride (70 mg) for 12 h. The mixture was evaporated, the residue was dissolved in dichloromethane (40 cm^3), and the solution was washed successively with 1 mol dm^{-3} hydrochloric acid (20 cm^3) and water (20 cm^3), dried, and evaporated. PLC [developer, dichloromethane–methyl acetate (9:1)] gave the *sulfonamides* **19** as an oil (92.5 mg, 61%). The two isomers (ratio 3:2) could be separated by extensive PLC [developer, ether–methyl acetate (9:1)]. The major, higher R_f, (Z)-*isomer* could be crystallized from ether–hexane as needles, m.p. 127–128 °C (Found: C, 59.0; H, 6.7; N, 6.4. $C_{31}H_{41}N_3O_9S$ requires C, 58.95; H, 6.55; N, 6.65%); λ_{max}(EtOH)/nm 229 and 281.4; ν_{max}/cm^{-1} 1720, 1660 and 1160 (SO_2); δ_H(D) 1.40 (6 H, s, CMe_2), 1.59 (9 H, s, Bu^t), 2.40 (3 H, s, PhMe), 2.42 (2 H, s, CH_2CON), 2.50 (2 H, m, $CH_2CH_2CO_2$), 2.90 (2 H, t, *J* 8, $CH_2CH_2CO_2$), 3.30 (2 H, br s, CH_2CO_2), 3.66 and 3.72 (each 3 H, s, OMe), 3.60–4.10 (2 H, m, CH_2N), 5.46 (1 H, br s, $NHSO_2$), 6.98 (1 H, br s, NH), 7.21 and 7.60 (each 2 H, d, *J* 8, ArH) and 8.52 (1 H, br s, NH); δ_C(D) 20.75 ($CH_2CH_2CO_2$), 21.49 (PhMe), 28.41 (CMe_3), 28.47 (CMe_2), 30.08 (CH_2CO_2), 34.93 ($CH_2CH_2CO_2$), 38.99 (CMe_2), 43.08 (CH_2CONH), 47.69 (CH_2NH), 51.46 and 52.51 (2 × OMe), 81.59 (CMe_3), 99.3 (C=CN), 116.26, 121.49, 128.75 and 128.89 (4 × pyrrole-C), 127.1 and 129.58 (aryl-CH), 136.85 (aryl-CMe), 143.37 (CSO_2), 151.31 (C=CN), 160.22 (CO_2Bu^t), 172.96 and 173.36 (CO_2Me), and 173.64 (CONH); *m*/*z* 631 (M^+, 100%). The minor, (E)-*isomer* was obtained as an oil (Found: M^+, 631.2574. $C_{31}H_{41}N_3O_9S$ requires *M*, 631.2563); λ_{max}(EtOH)/nm 228 and 276; ν_{max}/cm^{-1} 1725, 1660 and 1160 (SO_2); δ_H(D) 0.97 (6 H, s, CMe_2), 1.55 (9 H, s, Bu^t), 2.31 (2 H, s, CH_2CON), 2.40 (3 H, s, PhMe), 2.50 (2 H, m, $CH_2CH_2CO_2$), 2.96 (2 H, m, $CH_2CH_2CO_2$), 3.40 (2 H, br s, CH_2CO_2), 3.63 and 3.70 (each 3 H, s, OMe), 3.2–3.9 (2 H, m, CH_2NH), 6.42 (1 H, t, *J* 7, $NHSO_2$), 7.28 and 7.70 (each 2 H, d, *J* 8, Ar-H) and 8.41 and 8.48 (each 1 H, br s, NH); *m*/*z* 631 (M^+, 100%).

tert-*Butyl* (E)- *and* (Z)-8-(2-*Methoxycarbonylethyl*)-7-*methoxycarbonylmethyl*-3,3-*dimethyl*-1-*thioxo*-5-(p-*tolylsulfonylaminomethyl*)-1,2,3,10-*tetrahydrodipyrrin*-9-*carboxylate* **20**.—A stirred mixture of the isomers of lactam **19** (230 mg) and Lawesson's reagent (74 mg) were heated at reflux under argon for 10 min and was then evaporated. Filtration through silica [15 g; eluent, dichloromethane–methyl acetate (17:3)] gave the *sulfonamide thiolactams* **20** as an oil (225 mg, 95%). The two isomers (ratio 3:2) could be separated by extensive PLC [development several times with benzene–methyl acetate (9:1)]. The lower R_f band gave the major (Z)-*isomer* (Found: M^+, 647.2337. $C_{31}H_{41}N_3O_8S_2$ requires *M*, 647.2335); λ_{max}(EtOH)/nm 275 and 312; ν_{max}/cm^{-1} 1725, 1680, 1440 (C=S), 1330br (SO_2) and 1160 (SO_2); δ_H(C) 1.36 (6 H, s, CMe_2), 1.56 (9 H, s, Bu^t), 2.40 (3 H, s, PhMe), 2.51 (2 H, t, *J* 8, $CH_2CH_2CO_2$), 2.89 (2 H, s, CH_2CS), 2.90 (2 H, t, *J* 8, $CH_2CH_2CO_2$), 3.3 (2 H, m, CH_2CO_2), 3.66 and 3.71 (each 3 H, s, OMe), 3.81 (2 H, br s, CH_2NH), 5.51 (1 H, t, *J* 5, $NHSO_2$), 7.21 and 7.58 (each 2 H, d, *J* 8, ArH) and 8.51 and 8.78 (each 1 H, br s, NH); *m*/*z* 647 (M^+, 100%). The higher R_f band gave the (*E*)-isomer; λ_{max}(EtOH)/nm 304; ν_{max}/cm^{-1} 1725, 1675, 1430 (C=S), 1330br (SO_2) and 1160 (SO_2); δ_H(C) 0.92 (6 H, s, CMe_2), 1.53 (9 H, s, Bu^t), 2.40 (3 H, s, PhMe), 2.51 (2 H, t, *J* 8, $CH_2CH_2CO_2$), 2.77 (2 H, s, CH_2CS), 2.95 (2 H, t, *J* 8, $CH_2CH_2CO_2$), 3.4 (2 H, br s, CH_2CO_2), 3.63 and 3.70 (each 3 H, s, OMe), 3.6–3.8 (2 H, m, CH_2NH), 6.45 (1 H, t, *J* 7, CH_2NH), 7.28 and 7.72 (each 2 H, d, *J* 8, ArH) and 8.68 and 9.71 (each 1 H, br s, NH); *m*/*z* 647 (M^+, 100%).

tert-*Butyl* (E)- *and* (Z)-8-(2-*Methoxycarbonylethyl*)-7-*methoxycarbonylmethyl*-3,3-*dimethyl*-5-*methylsulfonylaminomethyl*-1-*oxo*-1,2,3,10-*tetrahydrodipyrrin*-9-*carboxylate* **21**.—The *meso*-cyano lactam **5** (53.8 mg) was stirred with W2 Raney nickel in methanol–water–methanesulfonic acid (80:19:1; 5 cm^3) under hydrogen for 3 h, then the mixture was filtered and the residue was washed with a mixture of methanol (100 cm^3) and pyridine (5 cm^3). The filtrate was evaporated, the residue was dissolved in toluene (10 cm^3), and the solution was evaporated. The residue was dissolved in dichloromethane (25 cm^3)–water (0.5 cm^3) and the organic layer was dried over magnesium sulfate and filtered. Methanesulfonyl chloride (80 mg) and 4-(dimethylamino)pyridine (150 mg) were added and the mixture was stirred for 15 min, washed successively with 1 mol dm^{-3} hydrochloric acid (2 × 20 cm^3) and 5% aq. sodium hydrogen carbonate (20 cm^3), dried and evaporated. PLC [developer, dichloromethane–methyl acetate (7:3)] gave the *sulfonamides* **21** as an oil (35.5 mg, 56%). The (E)- and (Z)-*isomers* could be separated by PLC for characterization (Found: M^+, 555.2252. $C_{25}H_{37}N_3O_9S$ requires *M*, 555.2250); λ_{max}($CHCl_3$)/nm 280; ν_{max}/cm^{-1} 3350br, 1720, 1660, 1320w (SO_2) and 1140 (SO_2); δ_H(B) [(*Z*)-isomer] 1.49 (6 H, s, CMe_2), 1.54 (9 H, s, Bu^t), 2.46 (2 H, s, 2-H_2), 2.50 (2 H, m, $CH_2CH_2CO_2$), 2.68 (3 H, s, SO_2Me), 2.85 (2 H, m, $CH_2CH_2CO_2$), 3.3 (2 H, br s, CH_2CO_2), 3.65 and 3.69 (each 3 H, s, OMe), 4.04 (2 H, d, *J* 6, CH_2NH), 5.38 (1 H, m, CH_2NH) and 7.18 and 9.27 (each 1 H, br s, NH); [(*E*)-isomer] 0.92 (6 H, s, CMe_2), 1.40 (9 H, s, Bu^t), 2.15 (2 H, s, 2-H_2), 2.30 (2 H, m, $CH_2CH_2CO_2$), 2.74 (3 H, s, SO_2Me), 2.78 (2 H, m, $CH_2CH_2CO_2$), 3.20 (2 H, br s, CH_2CO_2), 3.40 and 3.65 (each 3 H, s, OMe), 3.3–3.6 (2 H, br m, CH_2NH), 5.85 (1 H, br m, CH_2NH) and 9.3 and 9.9 (each 1 H, br s, NH); *m*/*z* 555 (M^+, 100%).

tert-*Butyl* (E)- *and* (Z)-5-*Acetamidomethyl*-8-(2-*methoxycarbonylethyl*)-7-*methoxycarbonylmethyl*-3,3-*dimethyl*-1-*oxo*-1,2,3,10-*tetrahydrodipyrrin*-9-*carboxylate* **22**.—The freshly prepared amine[2] **10** (40 mg) was stirred in pyridine (2 cm^3)–acetic anhydride (0.3 cm^3) for 40 min and the solution was then evaporated. A solution of the residue in dichloromethane (20 cm^3) was washed successively with dil. hydrochloric acid (2 × 20 cm^3) and 5% aq. sodium hydrogen carbonate (20 cm^3), dried, and evaporated. PLC [developer, dichloromethane–methyl acetate (7:3)] gave the *acetamides* **22** as oils [lower R_f, (Z)-*isomer*, 22 mg, 46%; higher R_f (E)-*isomer*, 6 mg, 14%] (Found: M^+, 519.2592. $C_{26}H_{37}N_3O_8$ requires *M*, 519.2580); λ_{max}($CHCl_3$)/nm 278; ν_{max}/cm^{-1} 3200br, 1720 and 1670; δ_H(B) [(*Z*)-isomer] 1.45 (6 H, s, CMe_2), 1.54 (9 H, s, Bu^t), 1.87 (3 H, s, Ac), 2.43 (2 H, s, 2-H_2), 2.50 (2 H, br t, *J* 8, $CH_2CH_2CO_2$), 2.90 (2 H, br t, *J* 8, $CH_2CH_2CO_2$), 3.30 (2 H, s, CH_2CO_2), 3.65 and 3.69 (each 3 H, s, OMe), 4.15 (2 H, d, *J* 6,

CH_2NH), 6.73 (1 H, br m, CH_2NH) and 7.0 and 9.1 (each 1 H, br s, NH); [(*E*)-isomer] 0.96 (6 H, s, CMe_2), 1.57 (9 H, s, Bu^t), 1.95 (3 H, s, Ac), 2.31 (2 H, s, 2-H_2), 2.50 (2 H, br t, *J* 8, $CH_2CH_2CO_2$), 2.90 (2 H, br t, *J* 8, $CH_2CH_2CO_2$), 3.35 (2 H, br s, CH_2CO_2), 3.65 and 3.66 (each 3 H, s, OMe), 3.73 (2 H, br s, CH_2NH) and 8.7 and 9.6 (each 1 H, br s, NH); *m/z* 519 (M^+, 100%).

tert-*Butyl* 8-(2-*Methoxycarbonylethyl*)-7-*methoxycarbonylmethyl*-3,3-*dimethyl*-1-*oxo*-1,2,3,10-*tetrahydrodipyrrin*-9-*carboxylate* **12**.—The methanesulfonamide **21** (16 mg), anisole (2 cm^3) and *N*,*N*′-dimethylethylenediamine (0.1 cm^3) were heated under argon at 110 °C for 8 h, and then the mixture was evaporated under high vacuum. PLC [developer, dichloromethane–methyl acetate (3:1)] gave the *meso*-free lactam[9] **12** as an oil (9.4 mg, 73%), shown by ^1H NMR spectroscopy to be solely the (*Z*)-isomer. A similar reaction on the toluene-*p*-sulfonamide **19** (10.6 mg) gave the same product (6 mg, 80%).

13,17-*Bis*-(2-*methoxycarbonylethyl*)-18-*methoxycarbonylmethyl*-2,2,8,8-*tetramethyl*-10^1,10^2-*dihydroazepino*[3,4,5-jk]*isobacteriochlorin*-10^3(10^4H)-*one* **18**.—The 10-cyanoisobacteriochlorin[2] **15** (4.0 mg) and zinc acetate (10 mg) were stirred in dichloromethane (0.5 cm^3)–methanol (5 cm^3) under argon for 30 min in the dark and the mixture was then evaporated. A solution of the residue in dichloromethane (5 cm^3) was washed with 5% aq. sodium hydrogen carbonate (2 cm^3), dried, and evaporated to afford the zinc isobacteriochlorin as a purple solid (4.1 mg, 94%), which was used directly in the next step; *m/z* 773, 775 and 777 (M^+, 30, 60 and 100%).

The zinc complex (4.1 mg) was dissolved in acetic acid (10 cm^3) and W2 Raney nickel (1 spatula tip) was added. The mixture was stirred under hydrogen for 26 h and then filtered through Celite, and the residue was washed with acetic acid (10 cm^3). The filtrate was evaporated, the residue was dissolved in dichloromethane (15 cm^3), and the solution was washed with 0.1 mol dm^{-3} hydrochloric acid (10 cm^3), dried and evaporated. PLC [developer, dichloromethane–methanol (9:1)] gave the *isobacteriochlorin lactam* **18** as a purple oil (2.5 mg, 58%) (Found: M^+, 683.3314. $C_{38}H_{45}N_5O_7$ requires *M*, 683.3318); $\lambda_{max}(CH_2Cl_2)$/nm 372, 548 and 591; ν_{max}/cm^{-1} 3300br, 1730 and 1600; δ_H(D) 1.66 and 1.82 (each 6 H, s, CMe_2), 2.86 and 2.93 (each 2 H, t, *J* 8, $CH_2CH_2CO_2$), 3.65 (9 H, s, 3 × OMe), 3.6–3.8 (4 H, m, 2 × $CH_2CH_2CO_2$), 3.70 and 3.72 (each 2 H, s, 3- and 7-H_2), 3.78 (2 H, s, CH_2CONH), 4.30 (2 H, s, CH_2CO_2), 5.2 (2 H, d, *J* 3.5, CH_2NH), 6.35 (1 H, t, *J* 3.5, CH_2NH), 6.78 (1 H, s, 5-H), 7.28 (1 H, s, 20-H) and 8.58 (1 H, s, 15-H); *m/z* 683 (M^+, 100%).

Reduction of the Zinc Complex of the 10-*Cyanoisobacteriochlorin* **15** *in TFA and TFAA*.—A solution of the isobacteriochlorin **15** (7 mg) in dichloromethane (3 cm^3)–methanol (5 cm^3) was stirred for 1 h under argon at 18 °C with zinc acetate (15 mg); TLC showed that complete conversion into the zinc complex had then occurred. A portion (2 mg) was dissolved in TFA (1 cm^3)–TFAA (0.2 cm^3) and the solution was stirred for 20 h under hydrogen at normal temperature and pressure with Raney nickel (~100 mg). The filtered solution was evaporated, the residue was dissolved in dichloromethane, and the solution was washed successively with 0.1 mol dm^{-3} hydrochloric acid and aq. sodium hydrogen carbonate. Fractionation of the material from the organic layer by PLC gave recovered **15** (~90% in different runs) together with the isobacteriochlorin **17** (3–5%), which was identified by mass spectrometry, *m/z* 683 (M^+), and by comparison with authentic material.[9]

(E)- *and* (Z)-8-(2-*Methoxycarbonylethyl*)-7-*methoxycarbonylmethyl*-3,3-*dimethyl*-1-*methylthio*-5-(p-*tolylsulfonylamino-methyl*)-2,3-*dihydrodipyrrin*-9-*carbaldehyde* **24**.—A mixture of the isomers of the sulfonamido thiolactam **20** (39.6 mg) was stirred in TFA (1 cm^3) under argon for 15 min. Trimethyl orthoformate (0.3 cm^3) was added followed, after 15 min by water (1.4 cm^3). After 30 min dichloromethane (20 cm^3) was added and the mixture was washed successively with 1 mol dm^{-3} aq. ammonia (30 cm^3) and water (20 cm^3), dried and evaporated. PLC [developer, dichloromethane–methanol (19:1)] gave the *thioimidate* **24** as an oil (13.0 mg, 30%), which could be seen from the ^1H NMR spectrum to be a mixture of two isomers (ratio >8:1). The major isomer was obtained pure by precipitation with methyl acetate–hexane, m.p. 111–113 °C (Found: M^+, 589.1921. $C_{28}H_{35}N_3O_7S_2$ requires *M*, 589.1916); λ_{max}(EtOH)/nm 226, 263 and 310; ν_{max}/cm^{-1} 3260br, 1740, 1680, 1310br (SO_2) and 1160 (SO_2); δ_H(D) 1.30 (6 H, s, CMe_2), 2.37 (3 H, s, SMe), 2.42 (3 H, s, Ph*Me*), 2.55 (2 H, t, *J* 7.6, $CH_2CH_2CO_2$), 2.71 (2 H, s, CH_2CS), 2.98 (2 H, t, *J* 7.6, $CH_2CH_2CO_2$), 3.45 (2 H, s, CH_2CO_2), 3.65 and 3.71 (each 3 H, s, OMe), 4.10 (2 H, d, *J* 4, CH_2NH), 5.85 (1 H, t, *J* 4, CH_2NH), 7.19 and 7.58 (each 2 H, d, ArH) and 9.98 (1 H, s, CHO); *m/z* 589 (M^+, 100%).

(Z)-8-(-2-*Methoxycarbonylethyl*)-7-*methoxycarbonylmethyl*-3,3-*dimethyl*-1-*methylthio*-2,3-*dihydrodipyrrin*-9-*carbaldehyde* **28**.—The thiolactam **13** (42.5 mg) was stirred in TFA (1 cm^3) under argon for 15 min. Trimethyl orthoformate (0.3 cm^3) was added, followed after 15 min by water (1.4 cm^3) and after a further 20 min by dichloromethane (20 cm^3) and 1 mol dm^{-3} aq. ammonia (25 cm^3). The organic layer was separated, dried, and evaporated. PLC [developer, ether–hexane, (2:1)] gave the *formyl thioimidate* **28** as fine yellow needles (16.0 mg, 43%), m.p. 91–92.5 °C (from ether–hexane) (Found: C, 59.0; H, 6.45; N, 6.8. $C_{20}H_{26}N_2O_5S$ requires C, 59.1; H, 6.45; N, 6.9%); λ_{max}/nm 389; ν_{max}/cm^{-1} 3320br, 1735 and 1625; δ_H(B) 1.27 (6 H, s, CMe_2), 2.60 (2 H, m, $CH_2CH_2CO_2$), 2.70 (2 H, s, CH_2CS), 2.72 (3 H, s, SMe), 3.03 (2 H, m, $CH_2CH_2CO_2$), 3.54 (2 H, s, CH_2CO_2), 3.66 and 3.68 (each 3 H, s, OMe), 5.68 (1 H, s, CH), 9.61 (1 H, s, CHO) and 11.6 (1 H, br s, NH); δ_C(D) 14.68 (SMe), 19.09 ($CH_2CH_2CO_2$), 28.79 (CMe_2), 29.79 (CH_2CO_2), 36.21 ($CH_2CH_2CO_2$), 43.20 (CMe_2), 51.66 and 52.06 (2 × OMe), 52.52 (CH_2CS), 97.80 (CH), 114.05, 128.68, 133.07 and 136.3 (4 × pyrrole-C), 165.75 (C=*C*N), 171.81 and 173.03 (2 × CO_2Me), 176.5 (CHO) and 181.28 (C=N); *m/z* 406 (M^+, 100%) and 347 (42).

13,17-*Bis*-(2-*methoxycarbonylethyl*)-12,18-*bis*(*methoxycarbonylmethyl*)-2,2,8,8-*tetramethylisobacteriochlorin* **17**.—See earlier for general directions for photochemical cyclizations. A portion of the foregoing product **28** was condensed with the imine **29** and the deeply coloured product, presumably **31**, was irradiated, these steps being carried out as for the strictly analogous oxygen systems **27** and **30**.[9] Work-up as for the oxygen series gave, in up to 40% yield, the isobacteriochlorin **17**, which was identified by direct comparison with an authentic sample.

8,12-*Bis*-(2-*methoxycarbonylethyl*)-7,13-*bis*(*methoxycarbonylmethyl*)-3,3,17,17,19-*pentamethyl*-2,3,17,18-*tetrahydrobilin*-1(2H)-*one* **32**.—The α-free imine[9] **29** (143 mg) and formyl lactam **26** (160 mg) were dissolved in methanol (40 cm^3). Methanol saturated with hydrogen chloride (1.0 cm^3) was added slowly to the stirred mixture. After 2 h no remaining α-free imine could be seen by TLC [dichloromethane–methyl acetate (9:1); staining with Ehrlich's reagent] and the mixture was evaporated, the residue was dissolved in dichloromethane (40 cm^3), and the solution was washed with 5% aq. sodium hydrogen carbonate (2 × 20 cm^3), dried, and evaporated. Chromatography on neutral alumina [activity I; 2 × 15 cm

column; eluent, dichloromethane–methyl acetate (9:1)] gave the *seco-lactam* **32** as purple prisms (190 mg, 65%), m.p. 111–112 °C (from methyl acetate–hexane) (Found: C, 64.3; H, 6.9; N, 7.8. $C_{38}H_{48}N_4O_9$ requires C, 64.75; H, 6.9; N, 7.95%); $\lambda_{max}(CH_2Cl_2)$/nm 322 and 568; [+$Zn(OAc)_2$ in MeOH] 332 and 650; ν_{max}/cm^{-1} 1740, 1635 and 1600; δ_H (D; CD_2Cl_2) 1.29 and 1.37 (each 6 H, s, CMe_2), 2.01 (3 H, s, N=CMe), 2.32 (2 H, s, CH_2C=N), 2.52 (2 H, s, CH_2CON), 2.59 (4 H, m, 2 × $CH_2CH_2CO_2$), 2.98 (4 H, m, 2 × $CH_2CH_2CO_2$), 3.56 and 3.60 (each 2 H, s, CH_2CO_2), 3.63, 3.65, 3.68 and 3.69 (each 3 H, s, OMe), 5.58 (1 H, s, 15-H), 5.89 (1 H, s, 5-H), 6.89 (1 H, s, 10-H) and 11.83 (1 H, br s, NH); δ_C(D) 19.56 and 19.90 (2 × $CH_2CH_2CO_2$), 20.99 (N=C*Me*), 29.01 and 29.53 (2 × CMe_2), 30.04 and 30.81 (2 × CH_2CO_2), 35.63 and 35.73 (2 × $CH_2CH_2CO_2$), 38.64 and 41.79 (2 × CMe_2), 44.58 (CH_2C=N), 51.50 and 53.40 (4 × OMe), 53.40 (CH_2CONH), 90.47 (C-15), 100.31 (C-5), 114.56 (C-10), 116.06, 127.20, 128.21, 131.97, 137.26, 144.52, 146.92 and 157.12 (8 × pyrrole-C), 164.08, 167.82 and 171.28 (2 × CNH and C=N) 171.69, 173.15, 174.65 and 174.64 (4 × CO_2) and 180.89 (CONH); *m*/*z* 704 (M^+, 100%).

8,12-*Bis*-(2-*methoxycarbonylethyl*)-7,13-*bis*(*methoxycarbonylmethyl*)-3,3,17,17,19-*pentamethyl*-2,3,17,18-*tetrahydrobilin*-1(2H)-*thione* **33**.—The seco-lactam **32** (10.0 mg) and Lawesson's reagent (3.15 mg) were stirred and heated at reflux in toluene (10 cm^3) for 10 min and the mixture was then evaporated. PLC [developer, dichloromethane–methyl acetate (9:1)] gave the seco-thiolactam **33** as a deep blue oil (9.6 mg, 94%); $\lambda_{max}(CH_2Cl_2)$/nm 300, 359 and 602; [+$Zn(OAc)_2$ in MeOH] 372 and 680; ν_{max}/cm^{-1} 3300br, 1730, 1640, 1600 and 1585; δ_H (D; CD_2Cl_2) 1.28 and 1.37 (each 6 H, s, CMe_2), 1.91 (3 H, s, N=CMe), 2.47 (2 H, s, CH_2C=N), 2.61 (4 H, m, 2 × $CH_2CH_2CO_2$), 2.86 (2 H, s, CH_2C=S), 3.04 (4 H, m, 2 × $CH_2CH_2CO_2$), 3.59 and 3.62 (each 2 H, s, CH_2CO_2), 3.63, 3.65, 3.67 and 3.69 (each 3 H, s, OMe), 5.71 (1 H, s, 15-H), 5.98 (1 H, s, 5-H), 7.04 (1 H, s, 10-H) and 11.6 (1 H, br s, NH); *m*/*z* 720 (M^+, 100%).

13,17-*Bis*-(2-*methoxycarbonylethyl*)-12,18-*bis*(*methoxycarbonylmethyl*)-2,2,8,8-*tetramethylisobacteriochlorin* **17**.—See earlier for general directions for photochemical cyclizations. The seco-thiolactam **33** (9.6 mg) was stirred under argon in TFA (1.0 cm^3)–trimethyl orthoformate (0.2 cm^3) for 20 min. The solvent was evaporated off under a stream of argon, tetrahydrofuran (30 cm^3) was added, and the solution was neutralized with Hünig's base until the colour had just turned from green to blue-purple, then was degassed, sealed under vacuum, and irradiated for 5 h. The residue obtained after evaporation was dissolved in dichloromethane (20 cm^3), and the solution was washed successively with 0.2 mol dm^{-3} hydrochloric acid (15 cm^3) and 5% aq. sodium hydrogen carbonate (15 cm^3), dried, and evaporated. PLC [developer, dichloromethane–methyl acetate (17:3)] gave the known[9] isobacteriochlorin **17** as a purple crystalline solid (7.5 mg, 82%), identified by comparison with an authentic sample.

Acknowledgements

Grateful acknowledgement is made to Dr P. R. Raithby (Cambridge) for the X-Ray analysis, the SERC for a Research Studentship (M. H. B.), to the National Science Foundation (USA) for a NATO Postdoctoral Fellowship (to S. C. Z.) and to the SERC, Roche Products Ltd. and Merck, Sharp & Dohme for financial support.

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Paper 2/02006H
Received 16*th April* 1992
Accepted 18*th May* 1992