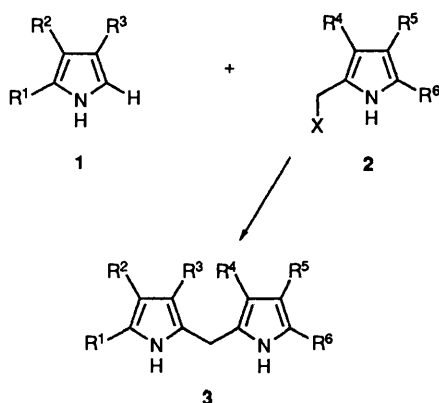


Selenomethylpyrroles: Their Use for Synthesis of Dipyrlylmethanes (Dipyrins), Tripyranes and Bilanes

Craig J. Hawker, Athena Philippides and Alan R. Battersby*
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK

Phenylselenomethylpyrroles react rapidly under mild conditions with α -free pyrroles in the presence of copper(I) triflate to form pyrrole-CH₂-pyrrole systems in preparative yields. The same coupling reaction can also be achieved thermally or photochemically but these approaches are limited in scope and, save for special cases, do not compete with the procedure based on copper(I).

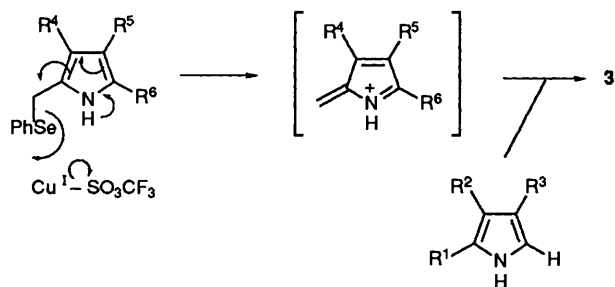
Molecules containing the system pyrrole-CH₂-pyrrole *e.g.* **3** have generally been synthesised as in Scheme 1 by joining a pyrrole having a free α -position **1** with a suitably substituted pyrrolomethyl system **2**. Commonly, group X has been acetoxy, the reaction being catalysed by protonic acids or Lewis acids such as tin(IV) chloride, but other X groups including halogen or amino groups have also been used.^{1,2}



Scheme 1

Our interest in the possible value of selenium for the type of chemistry summarised in Scheme 1 arose from the need, for other studies, to achieve this bond formation under mild and, if possible, essentially neutral conditions.

It was known that seleno esters generate acylium ions when treated with copper(I) salts³ and can be used in this way to acylate a range of aromatic systems. Accordingly, it seemed probable that by having X in Scheme 1 as SeR, then a selenophile such as copper(I) would promote the C-C bond formation as in Scheme 2 to yield the required systems. This paper reports the results of this study.



Scheme 2

Preparation of Selenomethylpyrroles.—Two methods were used to prepare the required selenium derivatives. Good to high

Table 1 Reactions of phenylselenomethylpyrroles with α -free pyrroles

Entry	Selenomethyl-pyrrole	α -Free pyrrole	Product	Yield (%)		
				Cu ^I	Thermal	<i>h</i> ν
1	5b	9a ^a	11a	60	56	57
2	5b	8	11d	56	61	0
3	5b	7	11b	71	19 ^c	0
4	5b	9b ^b	12a	72	76	70
5	5a	9a	11c	64	25 ^d	0
6	5a	8	11e	52	18 ^c	0
7	5a	7	11f	91 ^c	0	0
8	5a	9b	12b	50	0	0
9	5c	9a	12c	72	58	43
10	5c	8	12e	74	71	0
11	5c	7	12d	62	0	0
12	5c	9b	13b	51	36	—
13	5c	9c ^a	13a	—	—	36

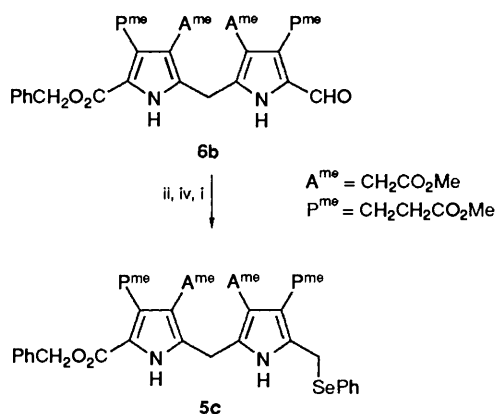
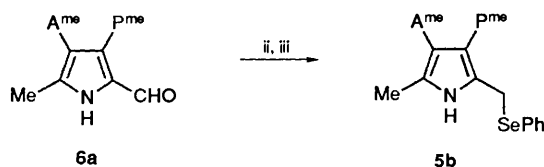
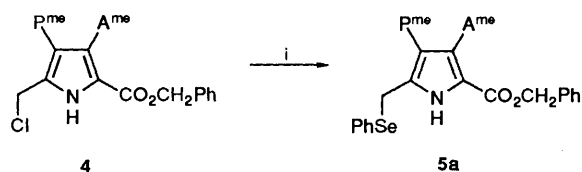
^a Ref. 7. ^b Ref. 8. ^c Reflux in dimethylformamide. ^d Reflux in toluene. ^e 5 min at -23 °C.

yields were routinely obtained by displacing halogen or methanesulphonyloxy groups with the selenophenolate anion, prepared in turn by borohydride reduction of diphenyl diselenide,⁴ see **4** \rightarrow **5a** and **6b** \rightarrow **5c**. The second method, *e.g.* **6a** \rightarrow **5b** involved reduction of a pyrrole aldehyde followed by treatment of the resultant alcohol directly with selenophenol and a catalytic quantity of toluene-*p*-sulphonic acid. For pyrroles without electron withdrawing groups *e.g.* **6a**, the latter method was the one of choice.

The phenylselenomethylpyrroles so prepared are light sensitive and must be protected from strong sunlight, but otherwise they are not difficult to handle.

Synthesis of Dipyrlylmethanes (Dipyrins) and Related Systems.—(a) *Use of Copper(I) triflate.* The simple procedure involved treatment of a solution of the α -free pyrrole and the phenylselenomethylpyrrole in dry degassed methylene dichloride containing calcium carbonate at -78 °C with a slight excess of the benzene complex of copper(I) triflate⁵ added in dry degassed benzene. The coupling reaction was very rapid and the product was isolated after 1–2 min at -78 °C. In one case, both reacting components carried an electron withdrawing group and then a longer reaction time at -23 °C was necessary. Table 1 collects the yields of dipyrlylmethanes synthesised by this method. Yields varying from satisfactory to good were obtained including many examples where the α -free pyrroles carried electron withdrawing groups.

Tripyranes were synthesised either by treating a selenomethylpyrrole, *e.g.* **5b**, with a dipyrlylmethane having a free α -position *e.g.* **9b** (Entry 4) or by combining a selenomethyl-di-



Reagents: i, PhSeH, DBU; ii, NaBH₄; iii, PhSeH, *p*-MeC₆H₄SO₃H; iv, MeSO₂Cl, -28 °C

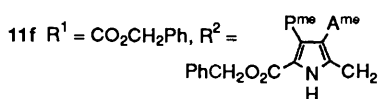
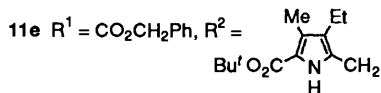
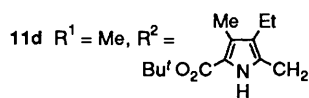
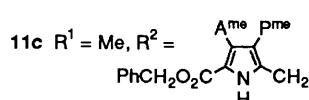
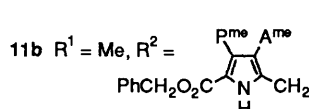
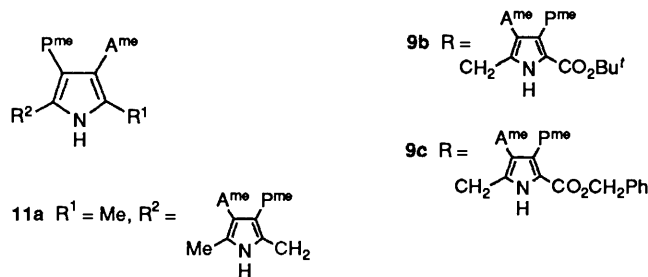
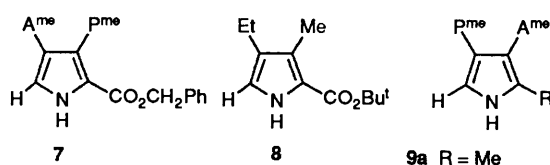
pyrrolmethane **5c** with an α -free pyrrole **9a** (Entry 9). Similarly, the two bilanes (Entries 12 and 13) were built by allowing a selenomethylpyrrole **5c** to react with a dipyrromethane having an α -free position **9b** or **9c**.

Calcium carbonate was included in the reaction mixture to remove the triflic acid released;³ no problems, such as cleavage of *tert*-butyl ester groups, were experienced. That the reaction was promoted by copper(I) and not by traces of triflic acid was proven by treatment of the α -free and phenylselenomethyl pyrroles with triflic acid under the condition used above; the starting materials were recovered unchanged.

(b) *Thermal coupling reactions.* It was found that the desired coupling could also be achieved thermally by heating the α -free pyrrole and the phenylselenomethylpyrrole under reflux in dry degassed benzene for 5 h. In three cases, higher temperatures were needed. This method works well when neither pyrrole involved is appreciably deactivated (see Entries 1, 2, 4, 9 and 10). The yields are poor when there is significant electron withdrawal from either pyrrolic component (Entries 3, 5, 6 and 12) and the thermal coupling fails if both pyrroles are deactivated (Entries 7, 8 and 11).

(c) *Photochemical coupling reactions.* We were interested to find that in some cases, the coupling of the two components could be carried out photochemically by irradiation of their solution in dry degassed benzene in the presence of triphenyltin hydride. No reaction occurred without irradiation. This approach is of limited scope since significant yields are only obtained when neither pyrrolic component is appreciably deactivated (Entries 1, 4, 9 and 13).

When the solvent for the photochemical reaction was dried but not degassed, considerable amounts of aldehyde (up to 50% yield) were formed from the phenylselenomethylpyrrole. Presumably this product arises by oxygen trapping the pyrrolomethyl radical followed by a hydrogen abstraction step and breakdown of the hydroperoxide **14** as in Scheme 3.



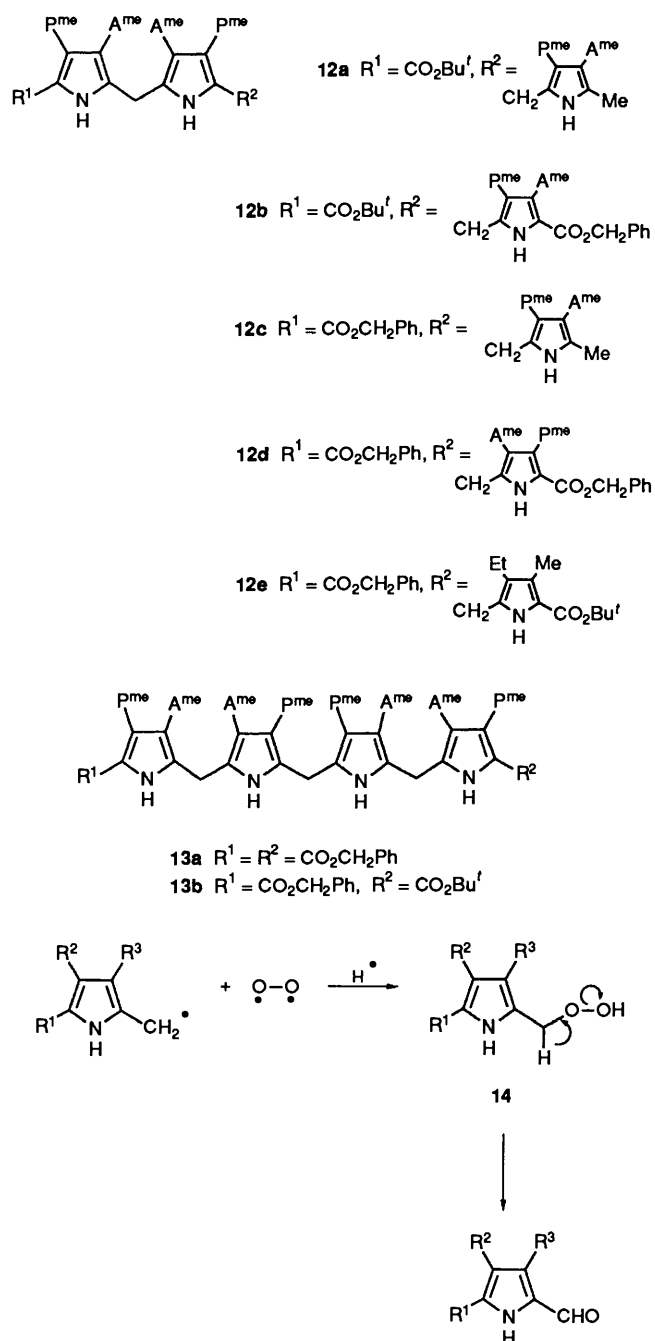
As a sideline to the photochemical studies, our expectation was confirmed that phenylselenomethylpyrroles can be reduced to methylpyrroles by irradiation in the presence of triphenyltin hydride, e.g. **5b** \rightarrow **10a** and **5a** \rightarrow **10b**. Alternatively, azo-isobutyronitrile (AIBN) can be used as the initiator and gave higher yields in the same two cases examined.

The outcome of this study is that the copper(I) promoted coupling process involving phenylselenomethylpyrroles is a useful, mild and essentially neutral procedure for the formation of pyrrole-CH₂-pyrrole systems.

Experimental

General directions are given in ref. 6. NMR spectra for both ¹H and ¹³C were run with solutions in CDCl₃ on a Bruker WH400 spectrometer and *J* values are given in Hz.

3-(2-Methoxycarbonylethyl)-4-methoxycarbonylmethyl-5-methyl-2-(phenylseleno)methylpyrrole **5b**.—To a stirred solution of the aldehyde **6a** (0.8 g) in dry dichloromethane (5 cm³) and methanol (10 cm³) was added sodium borohydride (114 mg) during 1 min under argon. The mixture was stirred at 18 °C for 10 min after which it was diluted with water (50 cm³) and extracted with dichloromethane (4 \times 15 cm³). The combined extracts were washed with saturated brine (30 cm³), dried and evaporated. The resultant alcohol was dissolved in dry degassed dichloromethane (25 cm³) and added dropwise to a stirred



Scheme 3

solution, in the same solvent (50 cm³), of selenophenol (3.76 g) and toluene-*p*-sulphonic acid (50 mg). After being stirred at 18 °C in the dark under argon for 16 h, the solution was washed with saturated aqueous sodium hydrogen carbonate (3 × 75 cm³) and water (75 cm³), dried and evaporated. Purification of the residue on silica (150 g) in 1:1 hexane-ether gave the *selenomethylpyrrole* as a yellow gum (733 mg, 60%) (Found: M^+ , 409.0775. C₁₉H₂₃NO₄⁸⁰Se requires M , 409.0792); δ_{H} 2.09 (3 H, s, CH₃), 2.35 and 2.58 (each 2 H, t, J 8, CH₂CH₂CO), 3.31 (2 H, s, CH₂CO), 3.61 and 3.62 (each 3 H, s, 2 × OMe), 4.05 (2 H, s, CH₂SePh) and 7.20–7.61 (5 H, m, Ph); δ_{C} 11.26, 19.56, 22.73, 30.20, 35.18, 51.47, 51.80, 110.80, 119.27, 122.05, 125.24, 127.41, 129.07, 131.44, 133.77, 172.70 and 173.71; m/z , cluster of peaks centred on 409 (⁸⁰Se), 100%.

Benzyl 4-(2-Methoxycarbonyl-ethyl)-3-methoxycarbonyl-methyl-5-(phenylseleno)methylpyrrole-2-carboxylate 5a.—A

solution of the chloromethylpyrrole¹⁰ **4** (0.5 g), selenophenol (0.96 g) and diazabicycloundecane (DBU) (0.48 g) in dry degassed chloroform (15 cm³) was heated at reflux under argon for 20 min then washed successively with saturated aqueous sodium hydrogen carbonate (3 × 15 cm³) and water (15 cm³) and then dried and evaporated. Chromatography of the product on silica (100 g) using 1:1 hexane-ether gave the title *phenylselenomethylpyrrole* (615 mg, 95%) (Found: M^+ , 529.0998. C₂₆H₂₇NO₆⁸⁰Se requires M , 529.1003); δ_{H} 2.37 and 2.59 (each 2 H, t, J 8, CH₂CH₂CO), 3.56 and 3.63 (each 3 H, s, 2 × OMe), 3.76 (2 H, s, CH₂CO), 4.03 (2 H, s, CH₂SePh), 5.24 (2 H, s, CH₂Ph), 7.17–7.21 and 7.32–7.41 (10 H, m, 2 × Ph) and 9.22 (1 H, br s, NH); δ_{C} 18.97, 21.65, 30.54, 34.62, 51.56, 51.79, 65.88, 118.65, 121.83, 127.63, 128.22, 128.29, 128.45, 129.11, 130.79, 131.39, 134.37, 135.89, 171.81 and 173.27; m/z , cluster of peaks centred on 529 (⁸⁰Se), 100%.

Benzyl 2,8-Bis(2-methoxycarbonyl-ethyl)-3,7-bis(methoxycarbonylmethyl)-9-(phenylseleno)methyl-5,10-dihydropyrrin-1-carboxylate 5c.—To a stirred solution of the aldehyde¹¹ **6b** (0.25 g) in dry dichloromethane (2.5 cm³) and methanol (5 cm³) under argon was added sodium borohydride (15.2 mg). After the mixture had been stirred at 18 °C for 10 min it was diluted with water (25 cm³) and the crude alcohol was isolated as for the preparation of **5b** above. It was dissolved in dry dichloromethane (5 cm³) containing triethylamine (0.2 cm³) and treated under argon at –23 °C with methanesulphonyl chloride (90 mm³) for 70 min. The solvent was then evaporated and the residue was stirred at 18 °C for 2 h with a solution of selenophenol (0.75 g) and DBU (0.16 g) in dry degassed chloroform (10 cm³). The rest of the work-up was as for **5b** above and yielded the title *compound* as a yellow gum (188 mg, 61%) (Found: M^+ , 766.2009. C₃₈H₄₂N₂O₁₀⁸⁰Se requires M , 766.2005); δ_{H} 2.24 and 3.02 (each 2 H, t, J 8, CH₂CH₂CO), 2.48–2.53 (4 H, m, CH₂CH₂CO), 3.42 and 3.55 (each 2 H, s, 2 × CH₂CO), 3.58, 3.61, 3.62 and 3.74 (each 3 H, s, 4 × OMe), 3.75 (2 H, s, CH₂-pyrrole), 4.01 (2 H, s, CH₂SePh), 5.25 (2 H, s, CH₂Ph), 7.11–7.14, 7.27–7.33 and 7.39–7.42 (10 H, m, 2 × Ph) and 9.28 and 10.23 (each 1 H, br s, 2 × NH); δ_{C} 19.24, 20.34, 22.25, 22.51, 29.21, 29.70, 34.65, 35.05, 51.29, 52.12, 52.34, 65.51, 110.47, 113.18, 117.64, 118.29, 123.73, 126.28, 127.13, 127.84, 128.25, 128.58, 129.69, 129.90, 133.36, 134.16, 136.08, 160.27, 173.40, 173.51, 173.88 and 174.14; m/z , cluster of peaks centred on 766 (⁸⁰Se), 100%.

General Method for Coupling Reaction using Copper(I) Triflate.—To a solution of the appropriate phenylselenomethylpyrrole (0.2 mmol) and α -free pyrrole (0.21 mmol) in dry degassed dichloromethane (5 cm³) containing powdered calcium carbonate (0.24 mmol) at –78 °C under argon was added the benzene complex of copper(I) triflate (0.12 mmol) in dry degassed benzene (0.5 cm³). The solution darkened immediately and after being stirred for 1–2 min at –78 °C, no selenomethylpyrrole remained (TLC). The mixture was poured into water (20 cm³), extracted with dichloromethane (4 × 10 cm³) and the combined extracts were washed with water (20 cm³) and dried. The product from evaporation of this solution was purified by PLC on silica using 1:9 hexane-ether.

General Method for Thermal Coupling Process.—The phenylselenomethylpyrrole (0.2 mmol) and the α -free pyrrole (0.21 mmol) were heated together in dry degassed benzene (10 cm³) under argon for 5 h and the product from evaporation was purified as in the foregoing method.

General Method for Photochemical Coupling Reaction.—The reaction mixture, prepared exactly as in the foregoing method, was stirred at 20 °C under argon whilst being irradiated with

UV light (Canrad-Hanovia 450 W mercury lamp). A solution of triphenyltin hydride (0.21 mmol) in dry degassed benzene (1 cm³) was slowly added during 8 h. The solution was then evaporated and the product was isolated as in the foregoing two examples.

Characterisation of Products.—The new materials from these experiments were characterised by elemental analysis or accurate mass measurement and by highfield NMR spectra for ¹H and ¹³C. The data for each substance are as follows.

3,7-Bis(2-methoxycarbonylethyl)-2,8-bis(methoxycarbonylmethyl)-1,9-dimethyl-5,10-dihydrodipyrin 11a.—(Found: M⁺, 490.2295. C₂₅H₃₄N₂O₈ requires M, 490.2315); δ_H 2.11 (6 H, s, 2 × CH₃), 2.56 and 2.77 (each 4 H, t, J 8, 2 × CH₂CH₂CO), 3.36 (4 H, s, 2 × CH₂CO), 3.63 and 3.66 (each 6 H, s, 4 × OMe), 3.76 (2 H, s, CH₂-pyrrole) and 8.24 (2 H, br s, 2 × NH); δ_C 10.89, 19.87, 20.95, 30.41, 35.10, 51.49, 51.75, 109.73, 116.26, 124.04, 124.32, 172.99 and 174.43.

Benzyl 2,7-Bis(2-methoxycarbonylethyl)-3,8-bis(methoxycarbonylmethyl)-9-methyl-5,10-dihydrodipyrin-1-carboxylate 11b.—(Found: C, 62.6; H, 6.4; N, 4.8. C₃₂H₃₈N₂O₁₀ requires C, 62.9; H, 6.3; N, 4.6%); δ_H 2.10 (3 H, s, C-Me), 2.47 and 2.59 (each 2 H, t, J 7, 2 × CH₂CH₂CO), 2.75 and 3.00 (each 2 H, t, J 6, 2 × CH₂CH₂CO), 3.36 and 3.56 (each 2 H, s, 2 × CH₂CO), 3.51, 3.61, 3.64 and 3.74 (each 3 H, s, 4 × OMe), 3.86 (2 H, s, CH₂-pyrrole), 5.24 (2 H, s, CH₂Ph), 7.28–7.38 (5 H, m, Ph) and 9.12 and 9.84 (each 1 H, br s, 2 × NH); δ_C 11.04, 18.96, 20.66, 22.07, 29.39, 29.62, 30.55, 34.59, 34.79, 35.65, 51.33, 51.66, 52.33, 65.65, 109.45, 113.91, 116.12, 117.75, 123.00, 125.00, 128.00, 128.22, 128.44, 130.04, 133.78, 136.21, 160.57, 172.83, 173.54, 174.30 and 174.87; m/z 610 (100%).

Benzyl 3,7-Bis(2-methoxycarbonylethyl)-2,8-bis(methoxycarbonylmethyl)-9-methyl-5,10-dihydrodipyrin-1-carboxylate 11c.—(Found: M⁺, 610.2529. C₃₂H₃₈N₂O₁₀ requires M, 610.2526); δ_H 2.10 (3 H, s, C-Me), 2.51–2.55 (4 H, m, 2 × CH₂CH₂CO), 2.74 and 2.78 (each 2 H, t, J 7, 2 × CH₂CH₂CO), 3.35 (2 H, s, CH₂CO), 3.54, 3.56, 3.63 and 3.65 (each 3 H, s, 4 × OMe), 3.80 and 3.88 (each 2 H, s, CH₂CO and CH₂-pyrrole), 5.21 (2 H, s, CH₂Ph), 7.30–7.35 (5 H, m, Ph) and 8.22 and 9.37 (each 1 H, br s, 2 × NH); δ_C 11.10, 19.21, 19.30, 22.23, 29.66, 30.45, 30.78, 34.68, 34.86, 51.62, 51.69, 51.80, 65.64, 109.98, 116.99, 119.94, 122.34, 122.36, 124.91, 128.06, 128.22, 128.42, 132.26, 136.01, 160.10, 171.13, 172.83, 173.21 and 174.35; m/z 610 (100%).

tert-Butyl 7-(2-Methoxycarbonylethyl)-8-methoxycarbonylmethyl-2,9-dimethyl-5,10-dihydrodipyrin-1-carboxylate 11d.—(Found: M⁺, 460.2571. C₂₅H₃₆N₂O₆ requires M, 460.2573); δ_H 1.05 (3 H, t, J 7, CH₂CH₃), 1.52 (9 H, s, CMe₃), 2.09 and 2.25 (each 3 H, s, 2 × CH₃), 2.41 (2 H, q, J 7, CH₂CH₃), 2.48 and 2.73 (each 2 H, t, J 7, CH₂CH₂CO), 3.36 (2 H, s, CH₂CO), 3.65 and 3.66 (each 3 H, s, 2 × OMe), 3.82 (2 H, s, CH₂-pyrrole) and 7.25 and 8.68 (each 1 H, br s, 2 × NH); δ_C 10.49, 11.15, 15.65, 17.17, 19.60, 22.45, 28.29, 28.50, 30.33, 35.25, 51.53, 51.74, 80.15, 110.61, 117.40, 118.99, 122.14, 123.84, 124.44, 125.64, 129.39, 161.35, 172.76 and 173.90; m/z 460 (100%).

1-tert-Butyl 9-Benzyl 3-Ethyl-7-(2-methoxycarbonylethyl)-8-methoxycarbonylmethyl-2-methyl-5,10-dihydrodipyrin-1,9-dicarboxylate 11e.—(Found: M⁺, 580.2788. C₃₂H₄₀N₂O₈ requires M, 580.2785); δ_H 1.02 (3 H, t, J 7, CH₂CH₃), 1.53 (9 H, s, CMe₃), 2.24 (3 H, s, C-Me), 2.35 (2 H, q, J 7, CH₂CH₃), 2.47 and 2.73 (each 2 H, t, J 7, CH₂CH₂CO), 3.57 and 3.64 (each 3 H, s, 2 × OMe), 3.76 and 3.89 (each 2 H, s, CH₂CO and CH₂-

pyrrole), 5.23 (2 H, s, CH₂Ph), 7.28–7.37 (5 H, m, Ph) and 8.56 and 8.74 (each 1 H, br s, 2 × NH); δ_C 10.53, 15.65, 17.25, 19.02, 22.82, 28.48, 30.72, 34.65, 51.80, 51.88, 65.89, 80.33, 114.78, 119.57, 120.52, 123.08, 124.36, 125.77, 127.12, 128.14, 128.21, 128.47, 130.90, 135.98, 161.26, 167.48, 172.78 and 173.55; m/z 580 (100%).

5,5'-Dibenzyl 2,7-Bis(2-methoxycarbonylethyl)-3,8-bis(methoxycarbonylmethyl)-5,10-dihydrodipyrin-1,9-dicarboxylate 11f.—(Found: M⁺, 730.2741. C₃₉H₄₂N₂O₁₂ requires M, 730.2738); δ_H 2.47, 2.57, 2.74 and 3.00 (each 2 H, t, J 7, 2 × CH₂-CH₂CO), 3.51, 3.59, 3.60 (each 3 H, s, 4 × OMe), 3.54 (2 H, s, CH₂CO), 3.79 and 3.93 (each 2 H, s, CH₂CO and CH₂-pyrrole), 5.22 and 5.24 (each 2 H, s, 2 × CH₂Ph), 7.27–7.38 (10 H, m, 2 × Ph) and 9.96 and 10.23 (each 1 H, br s, 2 × NH); δ_C 18.52, 20.55, 22.18, 29.32, 30.88, 34.13, 34.74, 51.41, 51.82, 51.90, 52.47, 65.52, 65.71, 114.54, 118.12, 119.13, 119.63, 122.54, 127.89, 128.06, 128.18, 128.29, 128.46, 128.89, 131.27, 131.97, 136.08, 136.24, 160.40, 160.48, 171.97, 173.55, 173.93 and 174.56; m/z 730 (100%).

tert-Butyl 2,8,12-Tris(2-methoxycarbonylethyl)-3,7,13-tris(methoxycarbonylmethyl)-14-methyl-5,10,15,17-tetrahydrotripyrin-1-carboxylate 12a.—(Found: M⁺, 813.3704. C₄₁H₅₅N₃O₁₄ requires M, 813.3684); δ_H 1.52 (9 H, s, CMe₃), 2.08 (3 H, s, C-Me), 2.42–2.46 and 2.71–2.75 (8 H, m, 2 × CH₂CH₂CO), 2.51 and 2.95 (each 2 H, t, J 7, CH₂CH₂CO), 3.33, 3.45 and 3.52 (each 2 H, s, 3 × CH₂CO), 3.60, 3.63, 3.63, 3.64, 3.67 and 3.74 (each 3 H, s, 6 × OMe), 3.71 and 3.74 (each 2 H, s, CH₂-pyrrole) and 8.11, 9.12 and 9.92 (each 1 H, br s, 3 × NH); δ_C 11.03, 19.56, 19.65, 20.46, 21.85, 22.15, 22.33, 28.31, 29.36, 29.91, 30.23, 34.91, 35.30, 35.47, 51.34, 51.45, 51.67, 52.30, 80.34, 109.86, 110.28, 112.79, 115.91, 116.51, 119.32, 123.46, 123.90, 125.27, 127.35, 128.39, 132.40, 160.32, 172.88, 173.69, 173.98 and 174.04; m/z 813 (100%).

1-Benzyl 14-tert-Butyl 3,7,13-Tris(2-methoxycarbonylethyl)-2,8,12-tris(methoxycarbonylmethyl)-5,10,15,17-tetrahydrotripyrin-1,14-dicarboxylate 12b.—(Found: M⁺, 933.3921. C₄₈H₅₉N₃O₁₆ requires M, 933.3895); δ_H 1.52 (9 H, s, CMe₃), 2.36–2.42 and 2.69–2.74 (8 H, m, 2 × CH₂CH₂CO), 2.51 and 2.95 (each 2 H, t, J 7, CH₂CH₂CO), 3.45 and 3.50 (each 3 H, s, 2 × CH₂CO), 3.51, 3.54, 3.57, 3.60, 3.61 and 3.74 (each 3 H, s, 6 × OMe), 3.63, 3.71 and 3.80 (each 2 H, s, CH₂CO and 2 × CH₂-pyrrole), 5.20 (2 H, s, CH₂Ph), 7.28–7.37 (5 H, m, Ph) and 9.20, 9.40 and 9.98 (each 1 H, br s, 3 × NH); δ_C 19.23, 19.41, 20.48, 20.60, 22.31, 22.63, 28.36, 29.40, 29.96, 30.68, 34.93, 35.20, 51.38, 51.52, 51.57, 51.72, 52.42, 52.47, 65.60, 80.32, 110.22, 112.83, 114.41, 116.51, 119.44, 120.43, 122.72, 123.51, 126.21, 128.05, 128.20, 128.30, 128.40, 132.10, 132.34, 136.17, 160.28, 160.64, 171.98, 173.44, 173.75, 173.88, 174.07 and 174.45; m/z 933 (100%).

Benzyl 2,8,12-Tris(2-methoxycarbonylethyl)-3,7,13-tris(methoxycarbonylmethyl)-14-methyl-5,10,15,17-tetrahydrotripyrin-1-carboxylate 12c.—(Found: M⁺, 847.3502. C₄₄H₅₃N₃O₁₄ requires M, 847.3528); δ_H 2.07 (3 H, s, C-Me), 2.28–2.41 and 2.68–2.72 (10 H, m, 2 × CH₂CH₂CO and CH₂-CH₂CO), 2.98 (2 H, t, J 7, CH₂CH₂CO), 3.32, 3.43 and 3.52 (each 2 H, s, 3 × CH₂CO), 3.59, 3.60, 3.60, 3.61, 3.63 and 3.66 (each 3 H, s, 6 × OMe), 3.70 and 3.74 (each 2 H, s, 2 × CH₂-pyrrole), 5.23 (s, 2 H, s, CH₂Ph), 7.30–7.38 (5 H, m, Ph) and 8.09, 9.12 and 10.11 (each 1 H, br s, 3 × NH); δ_C 11.10, 19.62, 19.71, 20.49, 22.24, 22.48, 29.38, 30.02, 30.31, 34.78, 35.35, 35.51, 51.38, 51.49, 51.70, 52.24, 52.36, 65.66, 109.98, 110.39, 113.28, 115.97, 116.65, 117.74, 123.48, 123.96, 125.20, 125.52, 127.98, 128.33, 128.39, 130.02, 133.60, 136.23, 160.46, 172.88, 173.61, 174.00 and 174.16; m/z 847 (100%).

Dibenzyl 2,8,13-Tris(2-methoxycarbonylethyl)-3,7,12-tris(methoxycarbonylmethyl)-5,10,15,17-tetrahydrotripyrin-1,14-dicarboxylate 12d.—M.p. 83–85 °C (Found: C, 63.2; H, 6.2; N, 4.6. C₅₁H₅₇N₃O₁₆ requires C, 63.3; H, 5.9; N, 4.3%); δ_{H} 2.44–2.50 and 2.94–2.98 (10 H, m, 2 × CH₂CH₂CO and CH₂CH₂CO), 2.69 (2 H, t, *J* 7, CH₂CH₂CO), 3.39, 3.48 and 3.52 (each 2 H, 3 × CH₂CO), 3.53, 3.56, 3.57, 3.59, 3.60 and 3.61 (each 3 H, s, 6 × OMe), 3.73 and 3.80 (each 2 H, s, 2 × CH₂-pyrrole), 5.22 and 5.23 (each 2 H, s, CH₂Ph), 7.29–7.39 (10 H, m, 2 × Ph) and 9.44, 9.58 and 9.93 (each 1 H, br s, 3 × NH); δ_{C} 19.01, 20.44, 20.55, 22.26, 22.38, 29.24, 29.33, 30.03, 34.65, 34.70, 51.25, 51.27, 51.57, 52.02, 52.09, 52.11, 65.52, 65.60, 110.24, 113.47, 113.98, 116.02, 117.53, 124.20, 125.49, 127.87, 127.97, 128.15, 128.33, 129.93, 130.00, 133.21, 133.44, 136.06, 136.16, 160.45, 160.56, 173.22, 173.43, 173.50, 173.54, 173.72 and 174.28; *m/z* 967 (100%).

1-Benzyl 14-tert-Butyl 2,8-Bis(2-methoxycarbonylethyl)-3,7-bis(methoxycarbonylmethyl)-12-ethyl-13-methyl-5,10,15,17-tetrahydrotripyrin-1,14-dicarboxylate 12e.—(Found: M⁺, 817.3741. C₄₄H₅₅N₃O₁₂ requires *M*, 817.3786); δ_{H} 0.93 (3 H, t, *J* 7, CH₂CH₃), 1.50 (9 H, s, CMe₃), 2.19 (3 H, s, C-Me), 2.33–2.37 (4 H, m, CH₂CH₂CO and CHCH₃), 2.48, 2.69 and 3.00 (each 2 H, t, *J* 7, CH₂CH₂CO and CH₂CH₂CO), 3.45 and 3.53 (each 2 H, s, 2 × CH₂CO), 3.53, 3.58, 3.61 and 3.64 (each 3 H, s, 4 × OMe), 3.73 and 3.74 (each 2 H, s, 2 × CH₂-pyrrole), 5.24 (2 H, s, CH₂Ph), 7.27–7.41 (5 H, m, Ph) and 8.61, 9.27 and 10.18 (each 1 H, br s, 3 × NH); δ_{C} 10.48, 15.35, 17.14, 19.59, 20.48, 22.41, 22.73, 28.49, 29.35, 29.99, 34.80, 35.46, 51.37, 51.54, 52.28, 52.47, 65.63, 79.90, 110.43, 113.22, 116.38, 117.80, 118.73, 123.57, 124.00, 125.44, 125.77, 127.95, 128.37, 129.61, 129.95, 133.67, 160.41, 161.50, 173.70 and 174.30; *m/z* 817 (100%).

Dibenzyl 2,8,12,18-Tetrakis(2-methoxycarbonylethyl)-3,7,13,17-tetrakis(methoxycarbonylmethyl)bilane-1,19-dicarboxylate 13a.—(Found: M⁺, 1204.4705. C₆₃H₇₂N₄O₂₀ requires *M*, 1204.4740); δ_{H} 2.20, 2.48, 2.63 and 2.98 (each 4 H, t, *J* 7, 4 × CH₂CH₂CO), 3.38 and 3.46 (each 4 H, s, 4 × CH₂CO), 3.56, 3.57, 3.66 and 3.62 (each 6 H, s, 8 × OMe), 3.67 (2 H, s, CH₂-pyrrole), 3.71 (4 H, s, 2 × CH₂-pyrrole), 5.23 (4 H, s, 2 × CH₂Ph), 7.26–7.39 (10 H, m, 2 × Ph) and 8.94 and 10.06 (each 2 H, br s, 4 × NH); *m/z* 1204 (100%).

1-Benzyl 19-tert-Butyl 2,8,12,18-Tetrakis(2-methoxycarbonylethyl)-3,7,13,17-tetrakis(methoxycarbonylmethyl)bilane-1,19-dicarboxylate 13b.—(Found: M⁺, 1170.4930. C₆₀H₇₄N₄O₂₀ requires *M*, 1170.4896); δ_{H} 1.51 (9 H, s, CMe₃), 2.22–2.26, 2.46–2.50, 2.64–2.68 and 2.90–2.96 (each 4 H, m, 4 × CH₂CH₂CO), 3.38, 3.39, 3.48 and 3.50 (each 2 H, s, 4 × CH₂CO), 3.57, 3.57, 3.60, 3.60, 3.61, 3.62, 3.64 and 3.72 (each 3 H, s, 8 × OMe), 3.67, 3.70 and 3.72 (each 2 H, s, 3 × CH₂-pyrrole), 5.23 (2 H, s, CH₂Ph), 7.29–7.39 (5 H, m, Ph), 8.93 (2 H, br s, 2 × NH) and 9.83 and 10.08 (each 1 H, br s, 2 × NH); δ_{C} 19.62, 20.52, 22.43, 22.77, 28.40, 29.37, 29.66, 29.94, 34.80, 35.01, 35.40, 51.37, 52.16, 52.27, 65.65, 80.38, 110.55, 112.96, 113.38, 113.70, 115.27, 116.30, 117.67, 119.37, 124.74, 124.88, 125.10, 125.26, 127.96, 128.31, 128.39, 136.02, 132.44, 133.66, 136.26, 160.39, 160.50, 173.62, 173.72, 173.83, 173.96 and 174.09; *m/z* 1170 (100%).

Reduction of Phenylselenomethylpyrroles.—(a) *The thermal method.* To a solution of triphenyltin hydride (94 mg) and AIBN (1 mg) in dry degassed benzene (2 cm³) heated at reflux was added a solution of the selenomethylpyrrole **5b** (34 mg), in dry degassed benzene (1 cm³), from a syringe pump during 30 min. After the mixture had been heated for a further 15 min, it was evaporated and the residue was purified by PLC using ether–hexane 7:3 to give the dimethylpyrrole **10a** as a colourless gum (14.7 mg, 70%) (Found: M⁺, 253.1311. C₁₃H₁₉NO₄ requires *M*, 253.1314); δ_{H} 2.13 and 2.14 (each 3 H, s, 2 × Me), 2.44 and 2.68 (each 2 H, t, *J* 8, CH₂CH₂CO), 3.37 (2 H, s, CH₂CO), 3.66 (6 H, s, 2 × OMe) and 7.53 (1 H, br s, NH); δ_{C} 11.03, 11.08, 19.88, 30.28, 35.47, 51.46, 51.81, 110.36, 116.65, 121.78, 122.95, 172.68 and 173.70; *m/z* 253 (100%).

The selenomethylpyrrole **5a** was similarly reduced to yield the pyrrole **10b**, 91%, m.p. 78–79 °C (lit.¹² m.p. 78.5–79.5 °C), shown to be identical with an authentic sample.

(b) *The photochemical method.* The selenomethylpyrrole **5b** (33 mg) in dry degassed benzene (1 cm³) was added from a syringe pump during 30 min to a stirred solution of triphenyltin hydride (137 mg) in dry degassed benzene (5 cm³) under argon which was irradiated with UV light as earlier. The solution was irradiated for a further 30 min after which it was evaporated and the product **10a** purified and identified as above (10.3 mg, 52%).

Similarly, **5a** was reduced to yield **10b** (80%) this being isolated and identified as before.

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