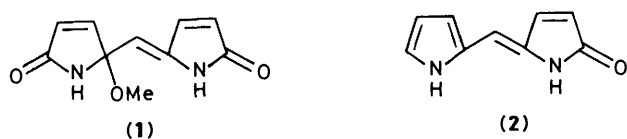


Propentdyopents and Related Compounds. Part 4.¹ Propentdyopent-Alkanol Adducts by the Photo-oxygenation of Pyrromethenones

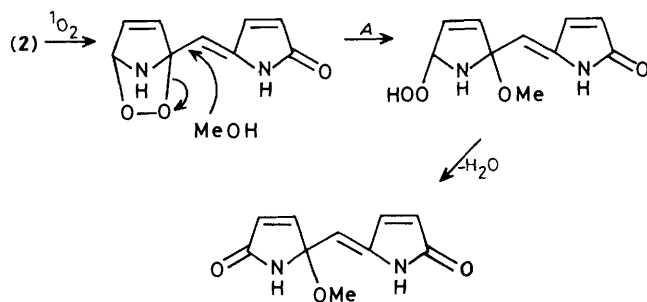
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Photo-oxygenation of tetraethylpyrromethenone and of tetramethylpyrromethenone in methanol in the presence of oxygen and a porphyrin photosensitiser gives the corresponding methanol-propentdyopent adducts in good yields. The photo-oxygenation reaction is shown not to be a satisfactory route to the analogous adducts with ethanol, propanol and butanol, but these compounds can be prepared by the acid-catalysed alcoholysis of the zinc(II) bis(tetra-alkylpropentdyopent) complexes. The photo-oxygenation is applied to [*meso*-¹³C]tetraethylpyrromethenone, and the result confirms the formulation of the methanol-propentdyopents as valley methoxy derivatives.

The low and irreproducible yields which bedevil the available preparative routes^{2,3} to the propentdyopent adducts have hampered the investigation of these compounds. We have devised a photochemical preparation which provides the intellectual satisfaction of being rational and which also gives improved yields for the methanol adducts. Moreover the new route has allowed experiments with ¹³C-labelled precursors, the results of which put beyond all reasonable doubt the 'valley' structure (1) for these substances.

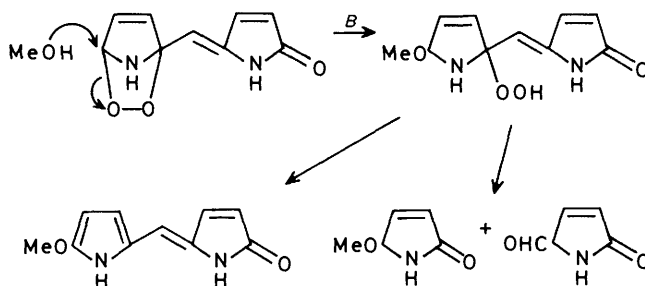


The starting materials are the pyrromethenones (2), the photochemical $Z \rightleftharpoons E$ isomerisation of which is well known.^{4,5} Although the photo-oxygenation of α -free pyrromethenones does not appear to have been reported, various α -alkylpyrromethenones have been studied in this way, with monopyrrole and dipyrrole derivatives being identified amongst the products.^{6,7} The auto-oxidation of α -alkylpyrromethenones on silica gel has been reported to give verdins, with propentdyopent adducts being formed as by-products.⁸ However, the photo-oxygenation of bilirubin IX α in methanol (either self-sensitised or in the presence of an exogenous photosensitiser) gives methanol-propentdyopent adducts as the major products. It was a consideration of the mechanism proposed for this reaction⁹ that led us to suppose that photo-oxygenation of α -free pyrromethenones in methanol might lead to the smooth generation of methanol-propentdyopent adducts, according to Scheme 1.



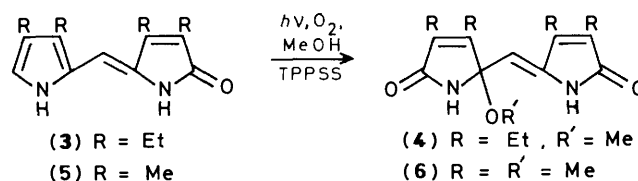
Scheme 1.

It was also envisaged that if nucleophilic attack occurred not at the bis-allylic centre (as in *A*), but at the less encumbered (but mono-allylic) α -position (as in *B*) then other products might be expected (Scheme 2).



Scheme 2.

A solution of tetraethylpyrromethenone (3) in dry methanol containing a trace of a water-soluble photosensitiser [tetra(*p*-hydroxysulphonylphenyl)porphyrin tetrasodium salt, TPPSS] and flushed with oxygen was irradiated with a 500W tungsten lamp for 20 min. By this time the pyrromethenone had disappeared: removal of the solvent, and of the photosensitiser by extraction into water from chloroform solution, gave tetraethyl(methanol)propentdyopent (4) as an amorphous solid in 94% yield (72% yield on crystallisation from chloroform-light petroleum). Rose Bengal could also be employed as a water-soluble photosensitiser, but gave lower yields under the conditions employed here.

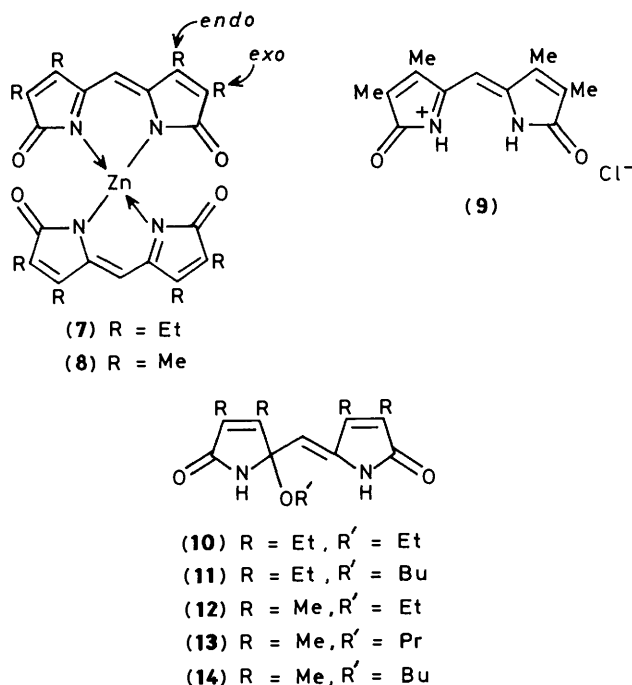


In the absence of exogenous photosensitiser, a slow photo-reaction occurred to give a mixture of products including the methanol adduct (4). Evidently the pyrromethenone (3) can sensitise its own photo-oxygenation, but the self-sensitised reaction is much the less efficient: a similar situation holds for bilirubin.^{10,11} In the absence of exogenous photosensitiser and oxygen, the only reaction observed on irradiation was the $Z \rightleftharpoons E$ isomerisation, which was followed chromatographically and by n.m.r. spectroscopy.

A similar photo-oxygenation occurred with the tetramethylpyrromethenone (5) in methanol to give the adduct (6) in 60% yield.

The reaction was also investigated with higher alcohols (EtOH, PrOH, BuOH). In all cases photoreaction occurred, but was slower, and mixtures of products, which included the corresponding alcohol and water adducts, were formed. We suppose that the extra steric requirement of the higher alcohols is causing the alternative pathway (Scheme 2) to compete effectively, leading to a mixture of products.

Authentic samples of the adducts of the three higher alcohols required for the foregoing experiments were prepared from the zinc complexes (7) and (8) by acid-catalysed solvolysis. With methanol this solvolysis proceeded smoothly to give (4) and (6) respectively. [The latter compound was also prepared by reacting methanol with the orange hydrochloride (9).] With ethanol, propanol, and butanol the analogous adducts (10)—(14) were obtained. They were more difficult to manipulate than were the methanol adducts, being subject to rapid discoloration on storage. Often they were produced along with minor amounts of the corresponding water adducts, which could generally be separated by chromatography. In the case of tetraethyl(propanol)propentdyopent this separation was not successful, and hence this substance is not described here.

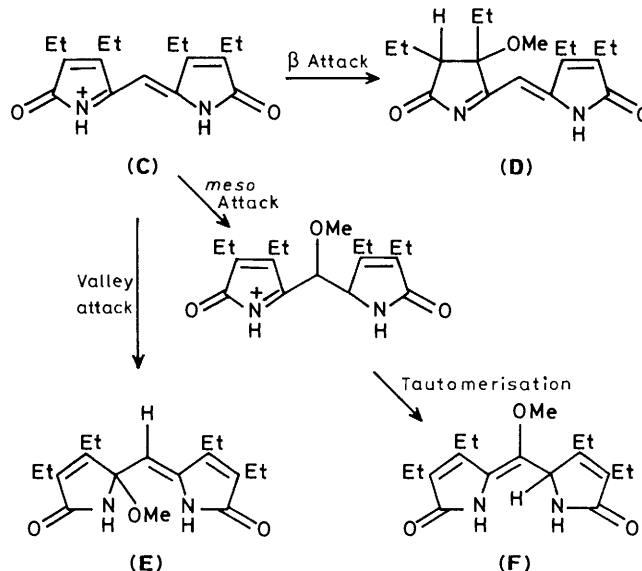


The new route to the methanol-propentdyopent adducts was used to confirm the valley structure^{2,3} [as in (1)] in the following way.

There is no ambiguity about the structure of (say) the zinc adduct (8) where the ¹H and ¹³C n.m.r. spectra indicate the symmetry shown. Thus in the ¹H n.m.r. spectrum of (8) there are two multiplets due to the two types of methyl groups, and the individual methyl groups can be assigned using the n.O.e. effect: irradiation at δ 5.70 (*meso*-proton) produces an enhancement at δ 2.08 but not at δ 1.84. Hence the former signal is attributed to the *endo*-methyl groups, and the latter to the *exo*-methyl groups.

The methanol adducts may be made by acid-catalysed solvolysis of the zinc complexes: the ¹H n.m.r. spectrum of the methanol adduct of tetraethylpropentdyopent showed a ¹H singlet at δ 4.72.

Solvolysis of the zinc complex, or the conjugate acid (C) of the corresponding free base might occur by one (or more) of the three routes shown in Scheme 3. Conjugate addition at the β-β' bond to give (D) is ruled out by the n.m.r. spectrum of the product: but the ¹H singlet at 4.72 just mentioned could be due to the *meso* proton of (E), arising from valley attack; or the valley proton of (F), arising from *meso* attack followed by tautomerisation (Scheme 3).



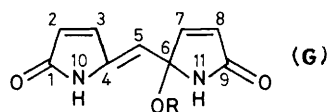
Scheme 3.

Because there are no close models for these unusual compounds, arguments based on ¹³C chemical shifts are also open to doubt. The ¹H decoupled ¹³C n.m.r. spectrum of tetraethyl(methanol)propentdyopent showed signals at δ 104.08 and δ 92.46 in the midfield region. In the off-resonance spectrum the signal at δ 104.08 (but not that at δ 92.46) was split into a doublet by the substituted hydrogen. The problem then reduced to discovering whether this signal represented the *meso*-carbon (as in E) or a highly deshielded valley carbon (as in F).

This problem was solved¹² by preparing a sample of tetraethyl(methanol)propentdyopent labelled at the *meso*-position with ¹³C. Formylation of 3,4-diethylpyrrole with [1-¹³C]dimethylformamide and condensation of the resulting aldehyde with 3,4-diethylpyrrol-2(*SH*)-one gave the [meso-¹³C]tetraethylpyrromethenone [(3) but *meso* ¹³C]. Photo-oxygenation as before gave the labelled methanol adduct, the ¹³C spectrum of which showed ¹³C enrichment at δ 103.93. This signal must, therefore, be due to the *meso*-carbon of the methanol adduct, and since it is split into a doublet in the off-resonance spectrum, the structure of tetraethyl(methanol)propentdyopent must be (E) and not (F). It is interesting to note that recent semi-empirical calculations on the reactivities of propentdyopent cations¹ accord with this experimental result.

Experimental

General.—Laboratory procedures were as previously described.^{3,5} The Stokvis reaction was carried out by treating a trace of the sample in methanol with 2M sodium hydroxide saturated with sodium dithionite. A pink colour (λ_{\max} , ca. 525 nm) at room temperature, or on gentle warming, indicated a positive result. The reaction could also be observed on silica gel plates by spraying with the same reagent. In n.m.r. assignments, positions are numbered on the extended system shown in (G).



Preparation of Tetraethyl(methanol)propentdyopent. [5-(3,4-Diethyl-5-methoxy-2-oxo-2,5-dihydropyrrol-5-ylmethylene)-3,4-diethylpyrrol-2(5H)-one] (**4**) by Photo-oxygenation of the Pyrromethenone (**3**).—5-(3,4-Diethylpyrrol-2-ylmethylene)-3,4-diethylpyrrol-2(5H)-one¹³ (63 mg) and 5,10,15,20-tetra(*p*-hydroxysulphonylphenyl)porphyrin tetrasodium salt (*ca.* 5 mg) were dissolved in anhydrous methanol (30 ml). A steady stream of oxygen was passed through the solution which was irradiated (500W tungsten lamp, 30 cm) at 10–15 °C. After 20 min the pyrromethenone had disappeared (t.l.c.), and the solvent was removed under reduced pressure. The residue was dissolved in chloroform (50 ml) and the solution quickly washed with water (3 × 25 ml) to remove the photosensitiser. The organic layer was dried (Na₂SO₄) and evaporated to yield crude tetraethyl(methanol)propentdyopent as a white amorphous solid (66 mg, 94%). Crystallisation from chloroform–light petroleum (b.p. 60–80 °C) gave the product (50 mg, 72%) as fine colourless crystals, m.p. 160–163 °C (decomp.) [lit.,³ m.p. 166–168 °C (decomp.)]; $\lambda_{\max.}(\text{CHCl}_3)$ 277 nm (26 000); m/z (e.i., 132 °C) 318.1955 (7%, M^+ , C₁₈H₂₆N₂O₃ requires 318.194), 303 (15, $M - 15$), 290 (22), 289 (100, $M - \text{Et}^?$, $M - \text{OMe} + 2\text{H}^?$), 287 (36, $M - \text{OMe}$), 259 (25), and 257 (33); (f.a.b., glycerol–tetrahydrofuran) 319 (15%, $M + \text{H}$) and 287 (100, $M - \text{OMe}$); $\delta_{\text{C}}(\text{CDCl}_3)$ 172.4, 171.5 (C-1, C-9), 154.8 (C-7), 145.8 (C-3), 140.1 (C-4), 136.7, 134.0 (C-2, C-8), 103.9 (C-5), 92.5 (C-6), 49.7 (OMe), 18.5, 17.6, 17.0, 16.8 (CH₂ of Et), 15.1, 13.5, 13.4, and 13.0 (CH₃ of Et).

(a) When the reaction was repeated in the absence of added photosensitiser, but with the reaction period extended to 2 h, t.l.c. showed that the pyrromethenone was not completely transformed, but that the methanol propentdyopent adduct and (in minor amount) the water adduct had both been formed. The reaction mixture gave a strong Stokvis reaction.

(b) In the absence of photosensitiser, irradiation as before but under nitrogen for 30 min, gave a second, more polar, yellow component, the *E*-isomer, which reverted to the starting material on two-dimensional chromatography on silica gel. Electronic spectroscopy showed only a small loss of absorption during photoisomerisation. The photoisomerisation was also carried out in an n.m.r. tube in CD₃OD: δ *meso*-H, 6.07 (*Z*) and 6.34 (*E*); α -H, 6.63 (*Z*) and 6.48 (*E*).

(c) Repetition of the sensitised photo-oxygenation in anhydrous ethanol was more complex. After 1 h the reaction was stopped, although the starting material had not completely disappeared, and worked up as before, to give a yellowish amorphous solid (~10%) which was a mixture of the ethanol (see below) and water adducts.

With anhydrous propanol as solvent the photoreaction gave a small amount of the water adduct. No propanol adduct was detected in this case.

Preparation of Tetraethyl(alkanol)propentdyopents by Solvolysis of the Zinc(II) Bis(tetraethylpropentdyopent) Complex (7).—(a) **Ethanol adduct.** To a stirred suspension of zinc(II) bis(tetraethylpropentdyopent)³ (30 mg, dried over P₂O₅ *in vacuo*) in dry ethanol (1.5 ml) was added a trace of dry trifluoroacetic acid. The mixture was stirred and warmed occasionally for 30 min, during which time the zinc complex had dissolved, and the solution had become cloudy. Addition of an excess of water and removal by filtration of the white precipitate without delay gave the *ethanol adduct* as a white amorphous solid (23 mg, 76%). Crystallisation from chloroform–hexane gave colourless micro-

crystals, m.p. 129–133 °C (decomp.) (Found: C, 68.1; H, 8.6; N, 8.4. C₁₉H₂₈N₂O₃ requires C, 68.65; H, 8.5; N, 8.45%); $\lambda_{\max.}(\text{CHCl}_3)$ 277 nm (29 000); $\nu_{\max.}(\text{KBr})$ 3 290w, 3 150w, and 1 650s cm⁻¹; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.20 (br, NH), 5.80 (br, NH), 4.71 (s, *meso*-H), 3.52, 3.21 (both m, 1 H each, OCH₂), 2.30 (m, =CCH₂CH₃), 1.26 (t, *J* 6.5 Hz, OCH₂CH₃), and 1.05 (m, =CCH₂CH₃); $\delta_{\text{C}}(\text{CDCl}_3)$ 172.2, 171.3 (C-1, C-9), 155.3 (C-7), 145.8 (C-3), 140.1 (C-4), 136.3, 133.9 (C-2, C-8), 104.1 (C-5), 92.1 (C-6), 58.0 (O-CH₃), 15.0, 13.5, 13.3, and 13.1 (CH₃ of C-Et); m/z (f.a.b., tetrahydrofuran–glycerol) 321 (100%, $M + \text{H}$).

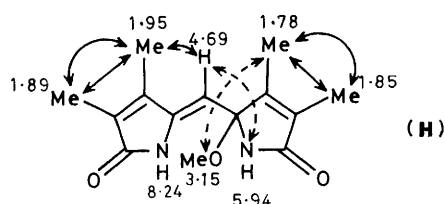
(b) **Butanol adduct.** An analogous experiment with butanol gave 60% of the *butanol adduct*, m.p. 118–124 °C (decomp.) (Found: C, 69.35; H, 9.5; N, 7.3. C₂₁H₃₂N₂O₃·0.5C₄H₉OH requires C, 69.5; H, 9.4; N, 7.05%); $\lambda_{\max.}(\text{CHCl}_3)$ 276 nm (20 600); $\nu_{\max.}(\text{KBr})$ 3 300–3 200br w, 1 690, and 1 655s cm⁻¹; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.17 (br, NH), 5.80 (br, NH), 4.71 (s, *meso*-H), 3.12, 3.45 (both, m, 1 H each, OCH₂), 2.15–2.4 (m, =CCH₂CH₃), 1.60 (m, OCH₂CH₂), 1.38 (m, OCH₂CH₂CH₂), 1.11 (m, =CCH₂CH₃), and 0.93 (t, *J* 8 Hz, OCH₂CH₂CH₂CH₃); m/z (e.i., 209 °C) 360.243 (3%, M^+ , C₂₁H₃₂N₂O₃ requires 360.241), 308 (28, $M - \text{C}_4\text{H}_9$), 288 (13), 287 (25, $M - \text{OC}_4\text{H}_9$), 275 (23), 259 (31), 258 (25), and 257 (100).

[¹³C]-Labelled Series.—3,4-Diethylpyrrole was formylated with [1-¹³C]dimethylformamide (16% isotopic enrichment) using the Vilsmeier reaction¹³ to give 3,4-diethyl-2-[¹³C]-formylpyrrole, m.p. 42–43 °C (lit.,¹³ m.p. 45 °C) in 41% yield. Condensation with 3,4-diethylpyrrol-2(5H)-one under basic conditions¹³ gave (37%) of the [*meso*-¹³C]tetraethylpyrromethenone, yellow needles, m.p. 172–174 °C from ethanol–water (lit.,¹⁴ m.p. 172.5–173 °C). The ¹³C n.m.r. spectrum showed ¹³C enrichment at δ 101.33 (*meso*-carbon).

Photo-oxygenation of the labelled pyrromethenone as described above gave (80%) the labelled methanol adduct, m.p. 155–157 °C (decomp.). The ¹³C n.m.r. spectrum showed ¹³C enrichment at δ 103.93. The ¹³C off-resonance spectrum showed a doublet at δ 104 and a quartet at δ 49.6.

Preparation of Tetramethyl(methanol)propentdyopent, [5-(5-Methoxy-3,4-dimethyl-2-oxo-2,5-dihydropyrrol-5-ylmethylene)-3,4-dimethylpyrrol-2(5H)-one] (6).—(a) **By photo-oxygenation.** 5-(3,4-Dimethylpyrrol-2-ylmethylene)-3,4-dimethylpyrrol-2(5H)-one¹⁴ [the pyrromethenone (**5**) (75 mg)] in anhydrous methanol (30 ml) containing 5,10,15,20-tetra(*p*-hydroxysulphonylphenyl)porphyrin tetrasodium salt (*ca.* 5 mg) was irradiated as before with oxygen flush for 30 min. The solvent was removed and the pink residue was dissolved in chloroform and washed with water. The organic layer was dried (MgSO₄), taken to dryness, and the crude pale yellow solid (71 mg) was crystallised from methanol to give the title methanol propentdyopent adduct (55 mg, 60%) as off-white crystals, m.p. 198–204 °C (decomp.) (lit.,¹⁵ m.p. 216–218 °C, decomp. from 160 °C); $\lambda_{\max.}(\text{MeOH})$ 274 nm (20 100); $\nu_{\max.}(\text{KBr})$ 3 350s, 3 220, 1 695s, 1 665s, 1 445, 1 380, 1 210, 1 180, 1 100, 1 060, and 1 010 cm⁻¹; m/z (f.a.b., 3-nitrobenzyl alcohol) 263.139 (9%, $M + \text{H}$, C₁₄H₁₈N₂O₃ + H requires 263.140) and 231 (100, $M + \text{H} - \text{MeOH}$); $\delta_{\text{H}}(\text{CDCl}_3)$, with expansion) 8.24 (br s, NH), 5.94 (br s, NH), 4.69 (s, *meso*-H), 3.15 (s, OMe), 1.95 (q, *J* 1 Hz, 3-Me), 1.89 (br q, *J* 1 Hz, 2-Me), 1.85 (q, *J* 1 Hz, 8-Me), and 1.78 (q, *J* 1 Hz, 7-Me). Decoupling and n.O.e. experiments were carried out on tetramethyl(methanol)propentdyopent, with the results indicated on structure (**H**). $\delta_{\text{C}}(\text{CDCl}_3)$ 173.0, 172.0 (C-1, C-9), 151.0 (C-7), 142.0 (C-3), 140 (C-4), 131.0, 129.2 (C-2, C-8), 103.8 (C-5), 93.0 (C-6), 49.7 (OMe), 10.29 (7-Me), 9.86 (3-Me), and 8.51 (2-Me, 8-Me).

(b) **From zinc(II) bis(tetramethylpropentdyopent).** The zinc(II) complex of tetramethylpropentdyopent¹⁵ was prepared as an orange-red solid (70% yield) by metallation of the foregoing



↔ coupling observed by decoupling experiment in each direction;
 ↷ strong n.o.e. effect; ↘ weak n.o.e. effect

methanolic adduct with zinc(II) acetate in refluxing methanol; $\lambda(\text{CHCl}_3)$ 360 (27 000), 490 (28 000), and 520 nm (27 000). $\nu_{\text{max.}}(\text{KBr})$ 1 710 and 1 525—1 510 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 5.70 (s, 2 \times 5-H), 2.08 (br s, 4 \times *endo*-Me), and 1.84 (br s, 4 \times *exo*-Me). Irradiation at δ 5.70 led to a large positive n.o.e. effect on the signal at δ 2.08.

A stirred suspension of the zinc complex (18 mg) in dry methanol (3 ml) containing trifluoroacetic acid (a few drops) was kept at *ca.* 50 °C for 1 h. The zinc complex gradually dissolved to give a colourless solution. The product was worked up through chloroform with aqueous washing. The dried chloroform solution was taken to dryness and the residue crystallised from methanol to give the methanol adduct (5.6 mg, 30%, m.p. 195—205 °C, decomp.) identical (t.l.c., i.r., ^1H n.m.r.) with the sample obtained above.

(c) *From the propentdyopent hydrochloride.* Tetramethyl-(methanol)propentdyopent (25 mg) in acetic acid (2 ml) was treated with an excess of anhydrous hydrogen chloride in diethyl ether until precipitation began. The mixture was left overnight at 4 °C. The orange precipitate was removed, washed with ether, and dried *in vacuo* to give tetramethylpropentdyopent hydrochloride¹⁶ (22 mg, 87%) as bright orange needles; $\lambda_{\text{max.}}(\text{CF}_3\text{CO}_2\text{H})$ 402 nm (8 000); $\nu_{\text{max.}}(\text{KBr})$ 3 400, 2 960, 2 820, 2 760, 2 620, 1 750, 1 690, 1 650, 1 590, 1 430, 1 380, 1 340, 1 250, 1 140, 1 020, 950, 790, 740, 710, 690, and 670 cm^{-1} ; $\delta_{\text{H}}(\text{CD}_3\text{CO}_2\text{D})$ 5.07 (s, *meso*-H), 1.88 (br s, 2 \times *endo*-Me), and 1.79 (br s, 2 \times *exo*-Me).

The orange hydrochloride (3 mg) was stirred in dry methanol (6 ml) at room temperature for 14 h. Removal of the solvent gave a discoloured solid (2 mg) which gave a positive Stokvis reaction and which was identical (t.l.c., u.v.) with the sample of tetramethyl(methanol)propentdyopent prepared by photo-oxygenation.

Photo-oxygenation of 5-(3,4-Dimethylpyrrol-2-ylmethylene)-3,4-dimethylpyrrol-2(5H)-one in other Alkanols.—The pyrromethenone (17 mg) in dry ethanol (45 ml) containing tetra[4-(*N*-methylpyridino)]porphyrin tetratoluene-*p*-sulphonate (3 mg) was irradiated as before for 1.5 h. The extraction procedure produced a brown oil (15 mg). This gave a strong Stokvis reaction and was shown to contain both ethanol and water adducts of tetramethylpropentdyopent (t.l.c., n.m.r.). However, it contained other components which could not be effectively separated.

Analogous results were observed when propanol and butanol were used as solvents.

Alkanolysis of Zinc(II) Bis(tetramethylpropentdyopent) (8) with other Alcohols.—The zinc complex (8) was treated in small scale experiments with various alcohols under conditions described for the methanolysis of this complex (above). The alkanol adducts were separated from minor amounts of the water adducts by preparative t.l.c. (silica gel; CHCl_3 –MeOH; 10:1) to give the following two adducts as white solids which became discoloured on storage. Ethanol adduct, m.p. 150—

160 °C (decomp.) (lit.,¹⁵ m.p. 214—218 °C, with decomp. from 140 °C); $\lambda_{\text{max.}}(\text{MeOH})$ 272 nm; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.17 (br s, NH), 5.92 (br s, NH), 4.68 (s, *meso*-H), 3.52, 3.17 (both, m, OCH_2), 1.95 (br s, 3-Me), 1.88 (br s, 2-Me), 1.83 (br s, 8-Me), 1.78 (br s, 7-Me), and 1.25 (m, OCH_2CH_3). *Propanol adduct*, m.p. 145—150 °C (decomp.); $\lambda_{\text{max.}}(\text{MeOH})$ 272 nm; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.13 (br s, NH), 5.86 (br s, NH), 4.68 (s, *meso*-H), *ca.* 3.4, 2.9 (both, m, OCH_2), 1.94 (br s, 3-Me), 1.88 (br s, 2-Me), 1.84 (br s, 8-Me), 1.79 (br s, 7-Me), 1.64 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$), and 0.92 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$). The *butanol adduct* was made as follows. The zinc complex (22 mg) was stirred in dry butanol (4 ml) containing a few drops of trifluoroacetic acid (*ca.* 40 °C, 1.5 h) until all the complex had dissolved. The solvent was removed and the oily residue was treated with light petroleum (b.p. 40—60 °C) to give the adduct as a pale yellow solid (13 mg, 57%), m.p. 140—145 °C (decomp.), which was a single substance on t.l.c. but which decomposed on storage; m/z (f.a.b., 3-nitrobenzyl alcohol) 305.187 (8%, $M + \text{H}$, $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_3 + \text{H}$ requires 305.187) and 231 (100, $M + 1 - \text{BuOH}$); $\lambda_{\text{max.}}(\text{MeOH})$, 274 nm (19 800); $\nu_{\text{max.}}(\text{KBr})$ 3 440, 1 690, 1 655, and 1 520 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.15 (br s, NH), 5.92 (br s, NH), 4.68 (s, *meso*-H), *ca.* 3.4, 3.1 (both, m, OCH_2), 1.96 (br s, 3-Me), 1.89 (br s, 2-Me), 1.84 (br s, 8-Me), 1.78 (br s, 7-Me), 1.60 (m, OCH_2CH_2), 1.38 (m, $\text{OCH}_2\text{CH}_2\text{CH}_2$), and 0.95 (t, 7.5 Hz, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

Acknowledgements

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References

- Part 3, R. Bonnett and M. A. Vallés, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1893.
- H. von Döbeneck in 'The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1979, Vol. 6, p. 651.
- R. Bonnett, M. J. Dimsdale, and G. F. Stephenson, *J. Chem. Soc., Perkin Trans. 1*, 1987, 439.
- H. Falk, K. Grubmayr, U. Herzig, and O. Hofer, *Tetrahedron Lett.*, 1975, 559.
- R. Bonnett, D. Hamzesh, and M. A. Vallés, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1383 and references therein.
- G. L. Landen, Y. T. Park, and D. A. Lightner, *Tetrahedron*, 1983, **38**, 1893.
- J. O. Grunewald, J. C. Walker, and E. R. Strobe, *Photochem. Photobiol.*, 1976, **24**, 29.
- D. A. Lightner and C. S. Pak, *Experientia*, 1976, **32**, 1107.
- R. Bonnett and J. C. M. Stewart, *J. Chem. Soc., Chem. Commun.*, 1972, 596.
- A. F. McDonagh, *Biochem. Biophys. Res. Commun.*, 1971, **44**, 1306.
- R. Bonnett and J. C. M. Stewart, *Biochem. J.*, 1972, **130**, 895.
- Preliminary communication: R. Bonnett and S. Ioannou, *J. Chem. Soc., Chem. Commun.*, 1986, 213.
- R. Bonnett, D. G. Buckley, and D. Hamzesh, *J. Chem. Soc., Perkin Trans. 1*, 1981, 322.
- H. von Döbeneck, W. Graf, and W. Ettl, *Hoppe Seyler's Z. Physiol. Chem.*, 1962, **329**, 168.
- H. von Döbeneck, D. Hägel, and W. Graf, *Hoppe Seyler's Z. Physiol. Chem.*, 1962, **329**, 182.
- H. von Döbeneck, E. Hägel, F. Schnierle, and E. Brunner, *Hoppe Seyler's Z. Physiol. Chem.*, 1965, **341**, 27.

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