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RHODIUM CATALYSED SYNTHESIS OF ILLUDALANES

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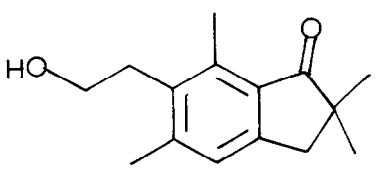
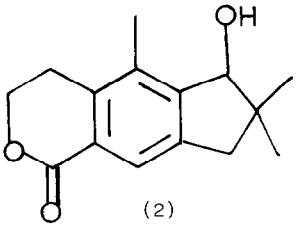
Abstract: A short, regiospecific route to pterosin Z and calomelanolactone is presented in which the key step is a rhodium catalysed intramolecular cycloaddition.

Pterosin Z (2) and calomelanolactone (1) are notable members of the illudalane class of sesquiterpenes.[1] Both have been isolated from the leaves of the silver fern Pityrogramma calomelanos[2]. Other members of the pterosin family, have been isolated from the Japanese fern pteridium aquilinium[3]. The exact role of these sesquiterpenes in plants is unknown, but it has been suggested that they may be involved in reproduction.



(1)

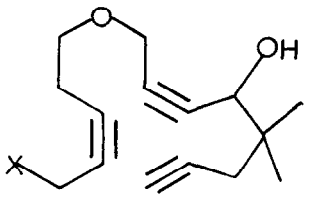


(2)

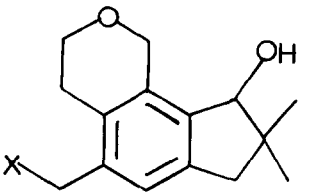
Highly substituted aromatic compounds, (particularly when all the substituents are different), are difficult to prepare using classical methodology. The major problem is that many of the reactions used, ie electrophilic substitution, and nucleophilic substition although regio-selective, are seldom regiospecific and isomer mixtures usually result. All reported syntheses of pterosins and illudalanes utilise intramolecular Friedel Crafts alkylation reactions[4].

Recently we have been developing new approaches to highly substituted aromatic compounds, based on rhodium catalysed [2+2+2] cyclo-additions[5]. A preliminary study has been published in which intramolecular rhodium catalysed [2+2+2], cycloadditions have been used in a short synthesis of calomelanolactone[6]. We now report full details of the synthesis of calomelanolactone and pterosin Z.

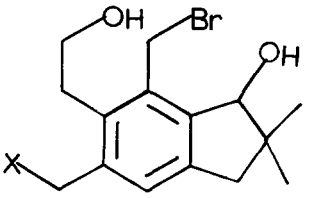
Synthetic strategy. Our strategy involved intramolecular trimerisations of the triacetylenes (3a,b) to give the tricyclic compounds (4a,b) followed by regiospecific ring opening of the cyclic benzylic ethers to give the key penta-substituted aromatic derivatives (5a,b). These were then converted to pterosin Z and calomelanolactone respectively.



3a X=H
3b X=OH



4a X=H
4b X=OH

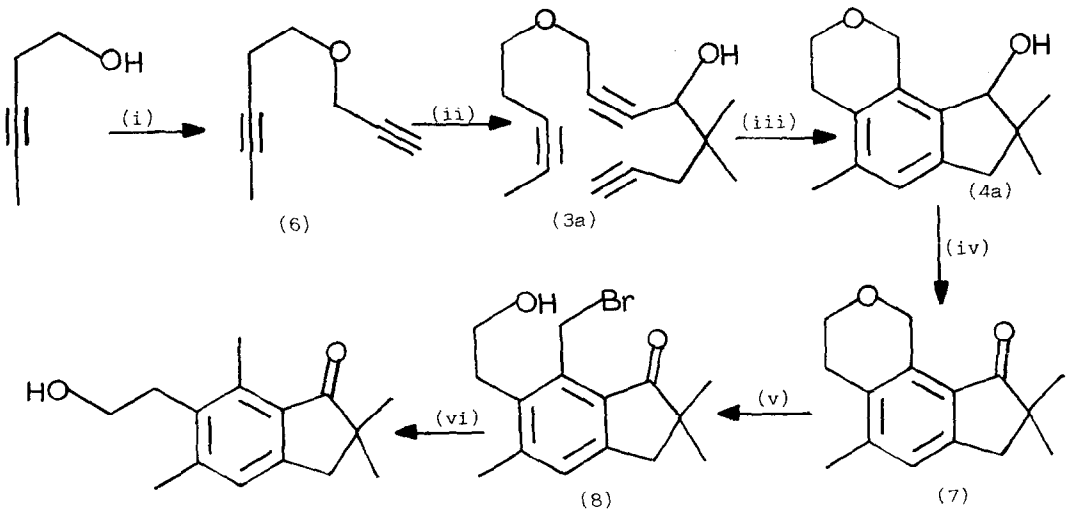


5a X=H
5b X=OH

Pterosin Z. The key triyne for pterosin Z (Scheme 1) was readily available from the propargyl ether of 3-pentyn-1-ol and 2,2-dimethyl-4-pentynal.[7] Hence the lithium acetylide of (6) smoothly condensed with 2,2-dimethyl-4-pentynal in THF at -78°C to give triyne (3a,76%) as a clear oil. It was surprising that this condensation proceeded so well, since the aldehyde has two α-methyl groups making it less reactive to nucleophilic attack, affording the possibility of acetylide equilibration, if the nucleophilic addition is slow. Triyne (3a) readily cyclised to give the tricyclic compound (4a, 82%) when treated with 2 mol % of Wilkinson's catalyst in ethanol at room temperature for 12hrs. The mechanism for this and similar reactions has been discussed elsewhere[5]. Oxidation of (4a) with pyridinium chlorochromate proceeded smoothly to give the tricyclic ketone (7, 84%).

Cleavage of the benzylic ether portion of (7) would at first seem a relatively simple task, but this reaction proved to be exceedingly difficult. Initially, catalytic hydrogenolysis was attempted using palladium on charcoal as the catalyst. However, under all conditions employed complex mixtures of reduction products resulted. Due to the failure of this one-step strategy, a two-step procedure involving ring opening followed by reduction of the benzylic halide was persued.

Treatment of (7) with a three molar excess of boron tribromide at -25°C in methylene chloride followed by heating at 40°C for 1 hr gave after workup (8), (62%). Surprisingly, trimethylsilyliodide[8] did not effect this cleavage. The cleavage was completely regiospecific , giving the benzylic bromide as the sole product. Finally, reduction of the benzylic bromide using tributyltin hydride gave Pterosin Z (51%) from (7).



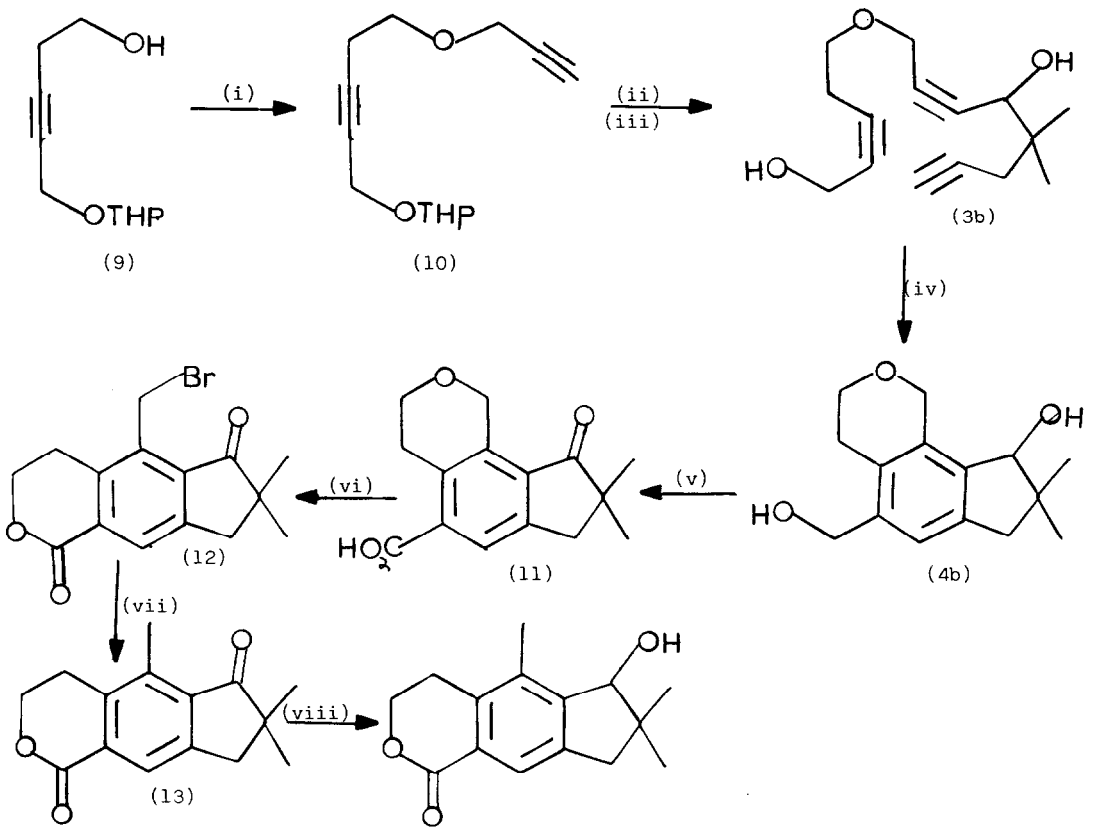
Reagents (i) sodium hydroxide, propargyl bromide, THF 60°C, (ii) BuLi, then 2,2-dimethyl-4-pentynal, (iii) 2 mol % Wilkinsons catalyst, EtOH, 12 h, 25°C, (iv) pyridinium chlorochromate methylene chloride, (v) BBr_3, (vi) tributyltin hydride, AIBN, benzene.

SCHEME 1

The synthesis of pterosin Z demonstrated the feasibility of this methodology. However, because two of the substituents on the aromatic ring are identical, pterosin Z is easy to obtain by other routes.[2] Calomelanolactone is a more challenging problem since all five substituents on the aromatic ring are different. This, coupled with the fact that no synthesis of calomelanolactone have to date been reported, made it an ideal molecule to test our methodology.

Calomelanolactone. The key triyne (3b) for calomelanolactone was obtained by condensing the lithium acetylide of (10) with 2,2-dimethyl-4-pentynal followed by mild acid hydrolysis of the THP protecting group.

(Scheme 2). Monoprotected alcohol (9) was obtained by the literature procedure[4] and was converted to its propargyl ether using sodium hydroxide as the base. The crucial trimerisation (3b → 4b) was again carried out in ethanol at room temperature using 2 mol % of Wilkinson's catalyst to give the tricyclic compound (4b), (86%). Oxidation using Jones' reagent in acetone at 0°C gave (11), (83%). Cleavage of the benzylic ether was again effected using boron tribromide and this resulted during work up in simultaneous lactonisation of the carboxy group to the hydroxy ethyl side chain to give (12), (85%). Tributyltin hydride reduction of the benzylic bromide followed by sodium borohydride reduction of the ketone gave calomelanolactone (1), (68%) overall from (12). Spectroscopic and physical data compared well with those reported in the literature.



Reagents (i) NaOH, propargyl bromide, THF, 60°C, (ii) Bu^nLi then 2,2-dimethyl-4-pentynal, (iii) MeOH, PTSA, (iv) 2 mol % $RhCl(PPh_3)_3$, EtOH, 12 h 25°C, (v) Jones Reagent, (vi) BBr_3, CH_2Cl_2, 3 h 35°, (vii) Bu_3SnH, AIBN, benzene, (vii) sodium borohydride.

SCHEME 2

In conclusion we have demonstrated that intramolecular trimerisation of propargyl ethers, followed by ether cleavage is a powerful method for the synthesis of multiblely substituted alkylindanes.

EXPERIMENTAL

Nmr spectra were recorded on Jeol 60 MHz and Bruker WM 250 MHz instruments in deuteriochloroform solution using tetramethylsilane as internal standard except where otherwise stated. Mass spectra were recorded on an AEI MS902 machine operating at 70 eV. Infrared spectra were recorded with a Perkin Elmer 475 spectrometer and refer to potassium bromide discs. M.p.s were determined on a Koeffler hot stage apparatus and are uncorrected.

4-oxa-nona-1,7-diyne (6). Propargyl bromide (19.3 g, 0.13 mol) was slowly added to a mechanically stirred suspension of powdered sodium hydroxide (5.76 g, 0.12 mol) and 3-pentyn-1-ol (10 g,0.12 mol) in dry THF(150 ml), and the resulting mixture was boiled under reflux overnight. The inorganic salts were removed by filtration and the THF was removed under reduced pressure. Water (30 ml) was added and this was extracted with ether (3 x 50 ml) dried over magnesium sulphate and concentrated to give a red oil. Distillation gave (6), (9.1 g, 66%) as a colourless oil bp 48-52^{o}C/2 mm Hg. (Found C, 78.38; H, 8.25. $C_8H_{10}O$ requires C, 78.65; H, 8.25%); δ4.18(2H, d, O-C$\underline{H}_2$-C); 3.60(2H, t, CH_2-C$\underline{H}_2$O); 2.44(3H, m, C≡C-H and C≡C-CH_2); 1.75(3H, t, C$\underline{H}_3$); ν_{max}(film) 3260, 2210, 1050: m/z (%) 122(M^+, 0.77), 107(50), 94(40), 69(37), 53(53), 39(100).

5-Hydroxy-4,4-dimethyl-9-oxatetradeca-1,6,12,-triyne(3a). N-Butyl lithium (11 ml 1.6 M, 17.6 mM) was slowly added to a stirred solution of (6, 2 g, 16.0 mmol) in anhydrous tetrahydrofuran (50 ml) under an atmosphere of dry nitrogen, and the mixture was kept in the temperature range -80 to -75^{o}C for 1 hr. The solution was allowed to warm to room temperature and then chilled again to -78^{o}C. 2,2-Dimethyl-4-pentynal (1.93 g, 17.6 m mol) was added dropwise keeping the temperature at -78^{o}C, and the solution was stirred at this temperature for a further hour. On warming to room temperature ammonium chloride solution (20 ml, 10%) was added, and most of the THF was removed under reduced pressure. The residue was extracted with ether (2 x 50 ml), dried over magnesium sulphate and concentrated. Distillation gave (3a), (2.83 g, 76%) as a viscous colourless oil b.p. 134-137^{o}C/0.2 mm Hg. (Found: C, 77.85 H, 9.01 $C_{15}H_{20}O_2$ requires: C, 77.55; H, 8.68%). δ4.31(1H, t, HO-C$\underline{H}$), 4.24(2H, d, O-C$\underline{H}_2$-C-C), 3.60(2H, t, CH_2-C$\underline{H}_2$-O), 2.44(2H, m, H_3C-C≡C-C$\underline{H}_2$), 2.24 and 2.36(2H, dd, H-C-C-C$\underline{H}_2$), 2.03(1H, t, C≡C-$\underline{H}$), 1.78(3H, t, C≡C-CH_3); ν_{max}(film) 3444, 3294, 2890, cm^{-1}; m/z (%), 232 (M^+, 2.5), 217 (17), 199 (20), 187 (31), 151 (28), 133

(21), 105 (25), 91 (26) 81 (100) and 41 (71).

2,2,5-Trimethyl-2'(H)-5',6'-dihydropyrano[3',4'-g] indan-1-ol(4a). Wilkinson's catalyst (80 mg, .09 mmol) was added to (3a), (1.0 g 4.3 mmol) in ethanol (30 ml) and the resulting suspension was stirred overnight under a nitrogen atmosphere. Removal of the solvent afforded a brown oil which was purified by column chromatography (solvent ether) to give (4a, 0.82 g 82%) as a white solid. Recrystallisation from ethanol gave (4a) as white prisms m.p. 83-85°C. (Found: C 77.25; H, 8.68. $C_{15}H_{20}O_2$ requires C, 77.55; H, 8.68%). δ6.87(1H, S, Ar-H), 4.98(1H, d, J = 15.5 Hz, Ar-CH_A H_B-O) 4.80(1H, d, J = 15.5 Hz Ar+CH_B H_A-O), 4.51(1H, s, CH-OH), 3.97(2H, m, CH_2-CH_2-O) 2.80(1H, d, J = 15.5 Hz Ar CH_A H_B C Me_2), 2.65(2H, m, Ar-CH_2 CH_2), 2.51(1H, d, J = 15 Hz Ar CH_B H_A-C Me_2) 2.18(3H, s, Ar-CH_3), 1.35(1H, br, OH), 1.14(3H, s, CH_3), 1.03(3H, s, CH_3); ν_{max} 3460, 3250, 1595 cm^{-1}; m/z (%) 232 (M^+, 25%), 214 (100), 199 (94), 91(10), 28 (49).

2,2,5-Trimethyl-2'(H)-5',6'-dihydropyrano [3',4'-g] indan-1-one (7). (4a), (0.42g, 1.81mmol) was added to a solution of pyridinium chlorochromate (0.58 g, 2.7 m mol) in anhydrous methylene chloride (10 ml) and the mixture was stirred at room temperature for 1 hr. Anhydrous ether (15 ml) was added and the dark liquid was decanted from the solid. The black residue was washed with ether (6 x 10 ml) and the extracts were combined with the supernatant. This was passed through a short column of florisil eluting with ether. Concentration of the colourless solution gave a gum which solidified on addition of petroleum ether. Crystallisation from ether: petroleum ether 2:1 gave (7), (0.35 g 84%) as colourless rods mp 78-80°C. (Found: C, 78.01; H, 7.65, $C_{15}H_{18}O_2$ requires: C, 78.26; H, 7.82%). δ 7.12(1H, s, Ar-H); 5.18(2H, s, Ar CH_2-O), 3.99(2H, t, O-CH_2-CH_2), 2.92(2H, s, Ar-CH_2-CMe_2). 2.72(2H, t, CH_2-CH_2 Ar), 2.31(3H, s, Ar-CH_3). 1.19(6H, s, 2 x CH_3); ν_{max} 2900, 1780, 1595: m/z (%) 230 (M^+ 100), 215 (88), 202 (12), 187 (29).

7-Bromomethyl-6-(2'-hydroxyethyl)-2,2,5-trimethylindan-1-one (8). Boron tribromide (13 ml) was added to a solution of (7), (1.0 g, 4.34 mmol) in anhydrous methylene chloride (20 ml) at a temperature of -25°C. After the addition the mixture was boiled under reflux for 1 hr. Neutralisation with sodium hydroxide solution, followed by washing with water (2 x 15 ml), drying ($MgSO_4$) and concentration gave a brown oil which solidified on trituration with ether. Recrystallisation from benzene gave (8), (0.83 g, 62%) as pale brown needles mp 96-98°C. (Found: C, 57.81; H, 6.33. $C_{15}H_{19}BrO_2$ requires: C, 57.87; H, 6.10%). δ 7.21(1H, s, Ar-H), 5.22(2H,s, Ar-CH_2-Br), 3.86(2H, t, CH_2-CH_2-OH), 3.14(2H, t, CH_2-CH_2-Ar), 2.86(2H, s, Ar CH_2 CMe_2), 2.72(1H, brs, O-H), 2.42(3H, s, Ar-CH_3), 1.20(6H, s, 2 x CH_3);

ν_{max} 3430, 2920, 1700, 1601 cm^{-1}. m/z (%) 312 (M^+ 35%),310 (M^+, 35%), 231 (100), 230 (36), 217 (28), 215 (59), 203 (58), 201 (48).

Pterosin Z (2) A solution of (8, 0.5 g, 1.61 mmol) tributyltin hydride (0.5 ml, 1.77 mmol) and AIBN (4 mg) in dry benzene (30 ml) was heated under reflux for 2 hrs. On cooling, the benzene solution was stirred overnight with 10 ml of a saturated solution of potassium fluoride in water. The solids were removed by filtration, the benzene dried over $MgSO_4$ and concentrated to give a brown oil. Column chromatography solvent pet ether/ether 70:30 gave an off-white solid (0.31 g, 83%) which was crystallised from benzene to give pterosin Z as needles mp 90-91°C (lit m.p. 86-88°C). (Found C, 77.88; H, 8.50; $C_{15}H_{20}O_2$ requires: C, 77.58; H, 8.62%), 7.04(1H, s, ArH), 3.72(2H, t, $C\underline{H}_2OH$) 2.82(2H, s, Ar-$C\underline{H}_2$-CMe_2), 2.65(3H, s, Ar-CH_3), 2.41(3H, s, Ar-CH_3), 2.18(1H, brs, O$\underline{H}$), 1.16(6H, s, 2 x $C\underline{H}_3$). ν_{max} 3433, 2890, 1675, 1598: m/z (%) 232 (M^+, 48), 218 (15), 201 (100), 189 (28), 28 (94).

Calomelanolactone (1)

1-(2'-Tetrahydropyranyloxy) -6-oxanona-2,8-diyne(10) Powdered sodium hydroxide (12.4% g, .31 mol) was added to a solution of 5-(2'-tetrahydropyranyloxy)-3-pentyn-1-ol (46 g, 0.25 mol) in anhydrous THF (300 ml) and the suspension was mechanically stirred for 1 hr. Propargyl bromide (35 ml, 0.31 mol) was added slowly and the vigorously stirred suspension was boiled under reflux for 12 hrs. Removal of the inorganic salts by filtration followed by evaporation of the solvent afforded a brown viscous oil. This was dissolved in ether (225 ml) and washed with water, dried $MgSO_4$ and concentrated. Distillation gave (10), (32 g, 58%) as a colourless oil b.p. 120-123°C/0.6 mm Hg. (Found: C, 69.71; H, 8.43 requires C, 70.24: H, 8.16%). δ 4.80(1H, t, O-C$\underline{H}$-O), 4.22(4H, m, C≡C-CH_2O), 3.66(2H, m, O-$C\underline{H}_2CH_2CH_2$), 3.65(2H, t, CH_2-$C\underline{H}_2$O) 2.54 (2H, m, C≡C-$C\underline{H}_2$-CH_2), 2.45(1H, t, C≡C-H), 1.51-1.85(6H, m, ring protons). ν_{max}(film) 3280, 2920, 2110, m/z (%) 222 (M^+ not observed), 101 (14), 91 (17), 85 (100).

1-(2'-Tetrahydropyranyloxy)-10-hydroxy-6-oxa-11,11-dimethyltetradecca-2,8,13-triyne (16) n-Butyl lithium (25.4 ml, 1.6 M sol, 40.7 m mol) was added dropwise to a stirred solution of (10), (8.2 g, 37 m mol) in anhydrous THF (100 ml) under at nitrogen atmosphere at 0°C. The solution was then cooled to -78°C and maintained at this temperature for 1 hr. 2,2-Dimethyl-4-pentynal (4.47 g 40.7 mmol) was added slowly and the mixture maintained at -78°C for a further 1 hr. On warming to room temperature saturated ammonium chloride solution (10 ml) was added. Most of the tetrahydrofuran was removed under reduced pressure and the residue was extracted with ether

(3 x 50 ml). Drying over magnesium sulphate followed by concentration gave a brown viscous oil. This was dissolved in methanol (50 ml) containing pyridinium p-toluenesulphonate (10 mg) and this was boiled under reflux for 1 hr. Removal of methanol followed by addition of water 20 ml and extraction with ether (3x50 ml), gave after concentration a brown oil. Short path distillation gave (3b), (8.4 g, 92%) as viscous colourless oil b.p. 140-143°C/0.05 mm Hg. (Found: C, 72.30; H, 8.27. $C_{15}H_{20}O_3$ requires: C, 72.58, H, 8.06%). δ 4.33(1H, t, HOC-H) 4.22(4H, m, HO-CH_2-C≡C and O-CH_2-C≡C), 3.65 (2H, t, O-CH_2CH_2), 2.54 (2H, m, C≡C-CH_2-CH_2), 2.38(1H, dd, C≡C-CH_A H_B C-Me_2), 2.22(H, dd, C≡C-CH_B H_A CMe_2), 2.03(2H, brs, 2xOH), 2.01(1H, t, S-C-H), 1.09(3H, S, CH_3), 1.08(3H, s, CH_3). ν_{max}(film) 3400, 3290, 2120; m/z (%) 248 (M^+, 11, 167 (28), 149 (18), 133 (22), 121 (22), 119 (25, 107 (17), 91 (51), 81 (100).

5-Hydroxymethyl-2,2-dimethyl-2'(H)-5',6'-dihydropyrano [3',4'-g] indanol (4b) Wilkinson's catalyst (74.4 mg, .08 mmol) was added to a stirred solution of (1b), (1g, 4.0 mmol) in ethanol (30 ml) and the resulting solution was stirred for twelve hours under a nitrogen atmosphere. Removal of the solvent followed by column chromatography (solvent ether) afforded a white solid (0.86 g, 86%). Crystallation from benzene gave (4b) as needles mp 148-150°C. (Found: C, 72.58; H, 8.10, $C_{15}H_{20}O_3$ requires C, 72.58; H, 8.06%). δ 7.10(1H, d, O-CH_A H_B-Ar), 4.65(2H, s, Ar-CH_2OH), 4.50(1H, s, HO-C-Ar) 3.99(2H, m, O-CH_2-CH_2), 2.81(2H, m, H_2C-CH_2-Ar), 2.80(1H, d, Ar-CH_A H_B-C-Me_2) 2.55(1H, d, Ar-CH_A H_B C-Me_2), 1.65(2H, brs, 2 x OH), 1.16(3H, s, CH_3), 1.05(3H, s, CH_3). ν_{max} 3534, 3295, 2910, 1456. m/z (%)48 (M^+, 3%) 230 (100), 215 (69), 129 (10), 91 (10).

5-Carboxyl-2,2-dimethyl-2'(H)-5',6'-dihydropyrano [3',4'-g] indan-1-one. (11) A solution of (4b), (1g, 4 mmol) in acetone (25 ml) was cooled to 0°C. Jones reagent was added dropwise until a permanent orange colour persisted. Excess reagent was destroyed by dropwise addition of isopropyl alcohol until a permanent green colour was observed. Removal of acetone in vacuo afforded a brown oil which was dissolved in ether (50 ml) and washed with water (3 x 10 ml). Drying over $MgSO_4$ followed by concentration gave a white powder which was crystallised from benzene to give (11), (0.86 g, 83%) as white needles m.p. 174-177°C. (Found: C, 69.03; H, 6.29; $C_{15}H_{16}O_4$ requires C, 69.23; H, 6.15%). δ 7.99(1H, s, Ar-H), 5.25(2H, s, O-CH_2-Ar), 3.98(2H, t, O-CH_2-CH_2), 3.26(2H, t, Ar-CH_2-CH_2), 3.03(2H, s, Ar-CH_2-C-Me_2), 1.24(6H, s, 2 x CH_3). ν_{max} 3407, 2912, 1712, 1697; m/z (%) 260 (M^+, 100), 245 (83), 217 (16), 28 (47).

5-Bromomethylcyclopenta [g]-6-one-7,7-dimethyl-3,4-dihydro-1 (H)-2-benzopyran-1-one (12) Boron tribromide (5.0 g, 20.8 mmol) was added

to a solution of (11) (1 g, 3.84 mmol), in anhydrous methylene chloride at -30°C. The resulting mixture was heated on a steam bath at 40°C for 1 hr. The reaction mixture was poured into water (10 ml), and extracted with methylene chloride (2 x 25 ml). The combined extracts were dried $MgSO_4$ and concentrated to give a brown oil which slowly crystallised. Recrystallisation from benzene gave (12), (0.93 g, 85%) as needles mp 175°C. (Found: C, 55.82; H, 4.68. $C_{15}H_{15}BrO_3$ requires: C, 55.72; H, 4.64%) δ 8.18(1H, s, Ar-H), 5.08(2H, s, Ar-CH_2-Br), 4.59(2H, t, O-CH_2-CH_2), 3.17(2H, t, Ar-CH_2-CH_2O), 3.02(2H, s, Ar-CH_2-C-Me_2), 1.26(6H, s, 2 x CH_3). ν_{max} 2980, 1726, 1710, 1607, 1294; m/z (%) 324 (M^+ 39), 322 (M^+ 40, 243 (100) 244 (31), 28 (98).

Cyclopenta [g]-6-one-5,7,7-trimethyl-3,4-dihydro-1 (H)-2-benzopyranone Tributyltin hydride (0.72 ml, 2.55 mmol) was added to a solution of (12) (0.75 g 2.32 mmol) and AIBN (5.7 mg .03 mmol) in dry benzene (30 ml) under a nitrogen atmosphere and the mixture was heated under reflux for 2 hrs. On cooling, the benzene was stirred with potassium fluoride (0.15 g, 2.55 mmol) in water 2 ml overnight. Removal of the inorganic salts and concentration of the dried benzene layer gave a brown oil. Column chromatography using ether gave white solid which was crystallised from benzene gave (13, 0.42 g, 75%) as white prisms m.p. 156-158°C. (Found: C, 73.65; H, 6.31. $C_{15}H_{16}O_3$ requires: C, 73.77; H 6.55%). δ 8.04(1H, s, Ar-H), 4.55(2H, t, O-CH_2-CH_2), 3.05(2H, t, Ar-CH_2-CH_2), 2.98(2H, s, Ar-CH_2-C-Me_2) 2,65(3H, s, Ar-CH_3), 1.23(6H, s, 2 x CH_3) ν_{max} 2890, 1715, 1701, 1605, 1254. m/z (%) 244 (M^+, 59%), 229 (100), 148 (25), 146 (25), 85 (21), 83 (13), 71 (35), 69 (42).

Calomelanolactone Sodium borohydride (16 mg, 04 mmol) was added to a solution of (13, 200 mg .82 mmol) in methanol (20 ml). When effervescence ceased (5 min) the solvent was removed, and the resulting gum was partitioned between ether (20 ml) and water 10 ml. The ethereal layer was dried and concentrated to give a pale yellow oil. Purification by preparative thin layer chromatography gave calomelanolactone (181 mg, 90%) as a colourless heavy oil. Attempt, to crystallise calomelanolactone were unsuccessful but spectroscopic data matched with that given by Bardouille.[2] (Found C, 73.17; H, 7.31%. $C_{15}H_{15}O_3$ requires: C 73.17; H, 7.31%). δ 7.73(1H, s, Ar-H) 4.57(1H, s, HC-OH), 4.42(2H, m, O-CH_2-CH_2O, 2.89(2H, m, Ar-CH_2-CH_2), 2.86(1H, d, Ar-CH_A-H_B-C-Me_2), 2.54(1H, d, Ar-CH_A-H_B-C-Me_2), 2.30(3H, s, Ar-CH_3O), 1.73(1H, brs, OH), 1.14(3H, s, CH_3), 0.93(3H, s, CH_3). ν_{max}(film) 3484, 1714, 1616, 1254, m/z (%) 246 (M^+, 96) 231 (100), 203 (41), 86 (95), 84 (93), 49 (24), 42 (16), 25 (20).

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