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SOME EXPERIMENTS WITH AMINODIHYDROXYANTHRAQUINONES†

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4-Amino-1-hydroxy-8-methoxyanthraquinone has been synthesised and alkylated with 1-nitropropane to give a mixture of 2- and 3-propyl compounds. Leuco-5-hydroxyquinizarin regioselectively reacts with n-propylamine and benzylamine to give 4-imino compounds, which are shown by ^{14}N n.m.r. spectroscopy to exist in solution as zwitterions. The benzylamine is regioselectively alkylated with propanal to give 4-benzylamino-1,5-dihydroxy-2-propylanthraquinone.

DUE to our interest in the synthesis of anthracyclinones[1] we have investigated the C-alkylation of some aminodihydroxyanthraquinone derivatives. Initially we synthesised the methoxy derivative (3) from the quinone[8] (1) by nitration with $Cu(NO_2)_2$-CF_3CO_2H which gave the nitro compound (2) accompanied by a small amount of an isomer. Reduction of the nitroquinone (2) with Zn-AcOH-CH_2Cl_2 gave the purple amino compound (3), the structure of which was established by reductive hydrolysis[2] ($Na_2S_2O_4$-NaOH) followed by aerial oxidation to give the known quinone (4). The minor isomer from the nitration was also reduced to an orange amine which could not be reductively hydrolysed. Its structure has not been definitely proven but the spectroscopic data are in accord with those anticipated for 2-amino-1-hydroxy-8-methoxyanthraquinone.

We have previously shown that 1,4,5-trihydroxyanthraquinone can be regiospecifically alkylated[3] at C-2 by Michael addition of a nitronate anion followed by *in situ* elimination of nitrite. Reaction of the amine (3) with 1-nitropropane in NaOMe-MeOH under the conditions developed previously did give propylated products but in lower yield (30%), at a slower rate and as a 5 : 2 mixture of products which could not be separated chromatographically. The major isomer (δ_H 7.11) was assigned structure (5) since the singlet aromatic proton was less shielded than in the minor isomer (6) (δ_H 6.85). The relatively poor yield and lack of regioselectivity in this reaction led us to abandon this approach. Our previous observations[4] that Marschalk condensation under Lewis conditions with leuco-derivatives of 2- and 3-alkyl-8-amino-1,4,5-trihydroxyanthraquinones led to regioselective 7-alkylation caused us to attempt to prepare the leuco-derivative of (3). Reduction of (3) with Zn-AcOH gave t.l.c. evidence of some reduction but attempts to isolate a pure product were thwarted by its very ready oxidation to starting material.

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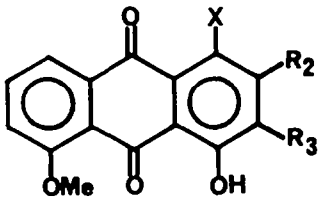
†This paper is dedicated to Professor R. A. Raphael on the occasion of his 65th birthday.



1 X = R_2 = R_3 = H

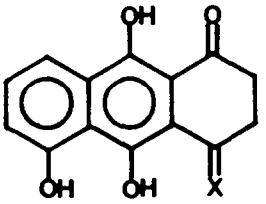
2 X = NO_2, R_2 = R_3 = H

3 X = NH_2, R_2 = R_3 = H

4 X = OH, R_2 = R_3 = H

5 X = NH_2, R_2 = n-Pr, R_3 = H

6 X = NH_2, R_2 = H, R_3 = n-Pr

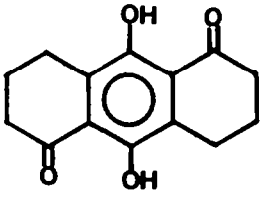


7 X = O

8 X = NPr^n

9 X = NBz

We then turned to the preparation of related leuco-compounds from leuco-1,4,5-trihydroxyanthraquinone (7) which reacted with Pr^nNH_2 and with $PhCH_2NH_2$ to give mono condensation products. Hydrolysis of both imines with 10MHCl or with 1.5MNaOH gave 5-hydroxyquinizarin after aerial oxidation of the hydrolysis mixtures. Both imines were oxidised to aminoanthraquinones on stirring in Et_3N-CH_2Cl_2 in the presence of air. The position of imine formation was indicated by reaction of both imines with pyrrolidine in PhMe[3] to give, in poor yield, 1,5-dihydroxyanthraquinone. Catalytic hydrogenation of the benzylimine



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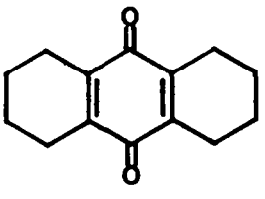

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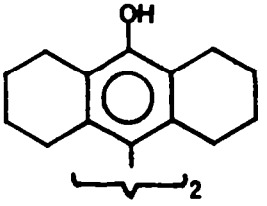

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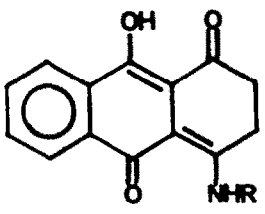
with Pt-H_2 in CH_3CO_2H also gave 1,5-dihydroxyanthraquinone, but as the minor product. The major compound had the composition $C_{14}H_{14}O_4$, δ_H 11.85 (2H, s), 2.85 (4H, bt), 2.64 (4H, m), 2.04 (4H, bt), ν_{max} 3400-2740, 1640 cm^{-1}, λ_{max} 240(3600), 282(5550), 292(5750), and 444(ε 1450) nm leading to its formulation as (10).# In support of this, the more rapid hydrogenation of 1,5-dihydroxyanthraquinone gave (10) as a minor product, the major one being the known[5] benzoquinone (11) accompanied by a dimeric compound formulated as (12) on the basis of analytical and spectroscopic data. All of the experiments described above support the formulation of the imines as (8) and (9). However, ^1H n.m.r. spectra do not support these structures in one important respect, the CH_2-N signal in the propyl compound is a quartet and a doublet in the benzyl. Decoupling established that the additional multiplicity was due to coupling with a low field proton not syn-anti isomerism. Previously mono-imine derivatives of leuco-1,4- dihydroxyanthraquinone have been prepared and, using a combination of ^1H and ^{13}C n.m.r. spectroscopy the 'non-aromatic' structure (14) proposed for these compounds;[6] however, in the case of our 5-hydroxyquinizarin derivatives we did not believe that the spectroscopic data allowed a clear distinction between the tautomer (of 14) and the zwitterion (13).



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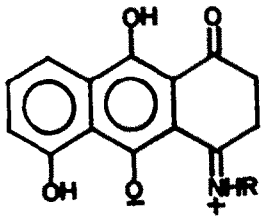

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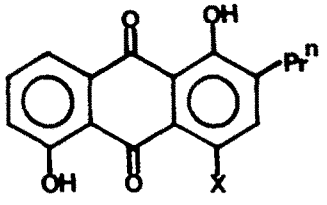
Such a distinction should be possible using ^{14}N n.m.r. spectroscopy and indeed a signal was observed at δ340 ppm from liquid NH_3 clearly indicating that the N was present in an iminium group,[7] and confirming the zwitterionic structure for (13) (R = Pr^n). The regioselective attack on the C-4 carbonyl group is in line with our previous observations[3] and is probably due to the more extensive hydrogen bonding array available to the intermediate formed by attack at C-4. Attempts to form the isomeric imine from the mono-anion of (7) were unsuccessful.



15 X = NHBz

16 X = NH_2

17 X = $NHPr^n$

18 X = H

Condensation of the benzyl imine (13, R = Bz) with propanal and piperidinium acetate in Me_2CHOH gave a single monoalkylated product in good yield. The chemical shift of the singlet proton (δ_H 7.00) did not allow determination of the position of alkylation; however, reduction with H_2-5%Pd-C gave an amine (δ_H 6.85) suggesting structure (16). Surprisingly, reduction-hydrolysis as applied to (3) gave only recovered starting material from the amines (15) and (16). Structure (17) was confirmed by reduction with Zn-AcOH to the dihydroxyanthraquinone (18), δ_H 7.83 (1H, d, J 8Hz), 7.29 (1H, d, J 8Hz); work-up of the reduction mixture gave (18) in a poor yield which was substantially improved by boiling the product mixture with 10MHCl before purification.

EXPERIMENTAL

N.M.R. spectra were measured on Varian SC300 and XL300 instruments

Nitration of the monomethyl ether (1).- Cupric nitrate (470 mg) was added in one portion to a stirred solution of monomethyl ether[8] (1) (500 mg) in CF_3CO_2H (16 ml) at room temperature. After 1.5 h the reaction was quenched by adding H_2O and the precipitate filtered off. Chromatography on silica eluting with 19 : 1 CH_2Cl_2 : EtOAc afforded two products. The major product was crystallised from EtOAc to give 4-hydroxy-5-methoxy-1-nitroanthraquinone (2) as orange crystals (350 mg) m.p. 215-217°C; ν_{max} ($CHCl_3$) 1680, 1640 cm^{-1}; λ_{max} ($CHCl_3$) 262(20,350), 280(11,980), 416(8250), 432(ε7500) nm; δ(300MHz, CD_2Cl_2) 13.38 (1H, s), 7.84 (2H, m), 7.65 (1H, d, J = 9Hz), 7.44 (1H, dd, J = 8 and 1.5 Hz), 7.34 (1H, d, J = 9 Hz), 4.02 (3H, s, OCH_3); (Found: C, 60.3; H, 2.9; N, 4.7 m/z 299.0428; $C_{15}H_9NO_6$ requires C, 60.2; H, 3.0; N, 4.7% m/z 299.0430).

The minor product was also crystallised from EtOAc to afford a nitro-compound as orange crystals (87.5 mg) m.p. 232-234°C, ν_{max} ($CHCl_3$) 1680, 1640 cm^{-1}; λ_{max} ($CHCl_3$) 254(19,300), 268(15,250), 280(11,975), 416(8000), 432(ε7020) nm; δ(300 MHz, CD_2Cl_2) 14.26 (1H, s), 8.23 (1H, d, J = 9 Hz), 7.99 (1H, dd, J = 8 and 1 Hz), 7.88 (1H, t, J = 8 Hz), 7.85 (1H, d, J = 9 Hz), 7.49 (1H, dd, J = 8 and 1 Hz), 4.06 (3H,s,OCH_3) (Found: C, 60.3; H, 2.9; N, 4.7 m/z 299.043; $C_{15}H_9NO_6$ requires C, 60.2; H, 2.9; N, 4.7%; m/z 299.0430).

4-Amino-1-hydroxy-8-methoxyanthraquinone.- Zinc dust (50 mg) followed by AcOH (10 ml) were added at room temperature to a stirred solution of 4-hydroxy-5-methoxy-1-nitroanthraquinone (2) (200 mg) in CH_2Cl_2 (80 ml). After 10 min the reaction mixture was filtered and the solution was washed with H_2O (150 ml), dried (Na_2SO_4), passed through a plug of silica and evaporated to give the pure product as a purple solid (160 mg), m.p. 236-238°C; ν_{max} ($CHCl_3$) 3675, 3490, 3320, 1620, 1600, 1590 cm^{-1}; λ_{max} ($CHCl_3$) 248(20,500), 284(8075), 380(2800), 506(8100), 523(9600), 564(ε6700) nm; δ(300 MHz, CD_2Cl_2) 13.84 (1H, s), 8.00 (1H, dd, J = 8 and 1 Hz), 7.76 (1H, t, J = 8 Hz), 7.31 (1H, dd, J = 8 and 1 Hz), 7.16 (1H, d, J = 9 Hz), 7.02 (1H, d, J = 9 Hz), 3.98 (3H, s) (m/z 269.0682: $C_{15}H_{11}NO_4$ requires 269.0688).

2-Amino-1-hydroxy-8-methoxyanthraquinone.- The same procedure was carried out as that in the previous experiment, except that the minor nitro-compound (50 mg) was used instead of (2). After work-up the amine was obtained as an orange solid (39 mg), m.p.251-253°C; ν_{max} ($CHCl_3$) 3680, 3510, 3415, 1660, 1610, 1585 cm^{-1}; λ_{max} ($CHCl_3$) 240(21,000), 256(26,110), 268(16,700), 288(10,100), 308(7700),394(5400), 472(ε6300) nm; δ(300 MHz, CD_2Cl_2) 13.44 (1H, s), 7.96 (1H, dd, J = 8 and 1 Hz), 7.77 (1H, t, J = 8 Hz), 7.71 (1H, d, J = 8.5 Hz), 7.36 (1H, dd, J = 8 and 1 Hz), 6.94 (1H, d, J = 8.5 Hz), 4.00 (3H, s); (m/z 269.0681; $C_{15}H_{11}NO_4$ requires 269.1681).

1,4-Dihydroxy-5-methoxyanthraquinone.- The hydrolysis was carried out using the method of Marshall.[2] $Na_2S_2O_4$ (1 g) in H_2O (5 ml) was added to a solution of amine (3) (30 mg) in 1.5MNaOH (50 ml). The solution was warmed at 90°C for 3 h during which a colour change from dark blue to yellow occurred. The solution was then aerated (20 min) until it had changed from yellow to dark blue; this was then acidified with 5MHCl. The reaction mixture was extracted with CH_2Cl_2(2 x 30 ml). The combined extracts were washed with H_2O (100 ml), dried (Na_2SO_4), passed through a plug of silica and then evaporated to give 1,4-dihydroxy-5-methoxyanthraquinone (24 mg), m.p. 193-195°C.

Alkylation of 4-amino-1-hydroxy-8-methoxyanthraquinone (3) with 1-nitropropane.- Amine (3) (30 mg) was dissolved in MeOH (50 ml) and a solution of NaOMe-MeOH (ex. 52 mg Na,MeOH 2 ml) was added in one portion. 1-Nitropropane (297.7 mg) was added and the solution was boiled under reflux for 48 h. The solution was then cooled to room temperature before being acidified with 2MHCl and extracted with CH_2Cl_2(2 x 30 ml). The combined extracts were washed with H_2O (100 ml), dried (Na_2SO_4) and evaporated to give a purple solid. T.l.c. on silica eluting with 19 : 1 CH_2Cl_2:EtOAc afforded the alkylated products as a purple solid (10.4 mg) m.p.153-155°C; ν_{max}($CHCl_3$) 3500, 3300, 2930, 2880, 1615, 1600, 1590 cm^{-1}; λ_{max} ($CHCl_3$) 242(21,000), 248(21,200), 284(7800), 376(2600), 504(6700), 534(8700), 572(ε6600) nm; δ(300 MHz, $CDCl_3$) (major isomer) 14.00 (1H, s), 8.08 (1H, dd, J = 8.4 and 1.2 Hz), 7.76 (1H, t, J = 8.4 Hz), 7.32 (1H, dd, J = 8.4 and 1.2 Hz), 7.11 (1H, s), 4.06 (3H, s), 2.55 (2H, t, J = 7.5 Hz), 1.72 (2H, m), 1.05 (3H, t, J = 7.5 Hz); (minor isomer) 14.42 (1H, s), 8.08 (1H, dd, J = 8.4 and 1.2 Hz), 7.76 (1H, t, J = 8.4 Hz), 7.32 (1H, dd, J = 8.4 and 1.2 Hz), 6.85 (1H, s), 4.06 (3H, s), 2.67 (2H, t, J = 7.5 Hz), 2.32 (2H, m), 0.99 (3H, t, J = 7.5 Hz); (m/z 311.1148; $C_{18}H_{17}NO_4$ requires 311.1157).

Preparation of the imine (8).- Pr^nNH_2 (236 mg) was added at room temperature to a stirred solution of leuco-1,4,5-trihydroxyanthraquinone (7) (1.032 g) in CH_2Cl_2 (350 ml) under a N_2 atmosphere. After 24 h the solvent was evaporated to give a yellow solid. Chromatography on silica eluting with 1 : 1 hexane: EtOAc afforded the imine (8) as a yellow solid (837.2 mg), m.p. 164-166°C; ν_{max} ($CHCl_3$) 2940, 2880, 1600, 1580 cm^{-1}; λ_{max} ($CHCl_3$) 260(34,000), 276(30,600), 420(11,600), 445(25,900), 474(ε35,200) nm; δ (300 MHz, CD_2Cl_2) 14.47 (1H, s), 13.89 (1H, s), 13.58 (1H, bs), 7.73 (1H, dd, J = 8 and 1 Hz), 7.56 (1H, t, J = 8 Hz), 7.00 (1H, dd, J = 8 and 1 Hz), 3.51 (2H, q), 3.03 (2H, t, J = 7.5 Hz), 2.84 (2H, t, J = 7.5 Hz), 1.79 (2H, m), 1.07 (3H, t, J = 7.5 Hz); δ_C (75.5 MHz, $CDCl_3$) 199.50, 176.00, 165.50, 162.50, 154.00, 132.50, 131.00, 120.00, 116.50, 115.00, 106.75, 101.00, 46.00, 34.50, 24.50, 23.00, 11.50; δ_N (21.7 MHz, $CDCl_3$) 340, (Found: C, 68.3; H, 5.5; N, 4.7, m/z 299.1150; $C_{17}H_{17}NO_4$ requires C, 68.2; H, 5.6; N, 4.7% m/z 299.1157).

Hydrolysis of imine (8).- (a) The imine (8) (20 mg) was boiled under reflux with 10M HCl (15 ml) for 2 h. The solution was diluted with H_2O (50 ml) and extracted with CH_2Cl_2 (2 x 30 ml). The combined extracts were washed with H_2O (100 ml), dried (Na_2SO_4) and evaporated to give a red solid (17 mg). T.l.c. on silica eluting with CH_2Cl_2 afforded 1,4,5-trihydroxyanthraquinone (10 mg).

(b) A suspension of the imine (8) (20 mg) in NaOH-H_2O (6% w/v, 50 ml) was heated at 90°C under a nitrogen atmosphere for 1 h. The mixture was cooled before being acidified with 10MHCl and extracted with CH_2Cl_2 (2 x 30 ml). The combined extracts were washed with H_2O (100 ml), dried (Na_2SO_4) and evaporated to give a blue solid (15 mg), consisting of an approximately equal mixture of 1,4,5-trihydroxyanthraquinone and 1,5-dihydroxy-4-propylaminoanthraquinone. T.l.c. on silica eluting with 1 : 1 CH_2Cl_2 : hexane afforded 1,4,5-trihydroxyanthraquinone as a red solid (6.5 mg).

Reaction of the imine (8) with pyrrolidine.- The imine (8) (50 mg) was dissolved in dry PhMe (35 ml) under a nitrogen atmosphere in a flask equipped with a Dean-Stark apparatus. Pyrrolidine (12 mg) in dry PhMe (4 ml) was added in one portion and the reaction mixture was boiled under reflux for 48 h. The solvent was evaporated to afford a blue solid (46 mg) consisting of starting material, 1,5-dihydroxy-4-propylaminoanthraquinone and 1,5-dihydroxy-anthraquinone. T.l.c. on silica eluting with dichloromethane gave 1,5-dihydroxyanthraquinone (4 mg), identical with an authentic specimen.

1,5-Dihydroxy-4-propylaminoanthraquinone.- A stirred solution of the imine (8) (50 mg) in CH_2Cl_2 (20 ml) was treated with Et_3N (1 ml) at room temperature. After 48 h the mixture was washed with 1MHCl (15 ml), H_2O (100 ml), dried (Na_2SO_4), passed through a plug of silica and evaporated to afford 1,5-dihydroxy-4-propylamino anthraquinone (45 mg) as a purple solid m.p. 185-187°C; ν_{max} ($CHCl_3$) 1590 cm^{-1}; λ_{max} ($CHCl_3$) 240(17,100), 252(12,267), 290(3903), 388(882), 534(4832), 592(8736), 614(ε8810) nm; δ(300 MHz, CD_2Cl_2) 13.90 (1H, s), 13.34 (1H, s), 10.01(1H, bs),7.82 (1H, dd, J = 8 and 1Hz), 7.60 (1H, t, J = 8Hz), 7.24 (3H, m), 3.35 (2H, q), 1.74 (2H, m), 1.02 (3H, t, J = 7.5Hz); (m/z 297.1001; $C_{17}H_{15}NO_4$ requires 297.1001).

Preparation of the imine (9).- The same procedure was carried out as that in the preparation of the propyl imine, except that the benzylamine (428 mg) was used instead of propylamine and the reaction mixture was boiled under reflux for 24 h. Usual work-up and chromatography eluting with 19 : 1 CH_2Cl_2: EtOAc afforded the imine (9) as yellow crystals (805 mg), m.p. 197-199°C; ν_{max} ($CHCl_3$) 1600, 1580 cm^{-1}; λ_{max} ($CHCl_3$) 258(27,500), 278(26,086), 400(5217), 420(10,869), 444(23,478), 474(ε32,065) nm; δ (300 MHz, $CDCl_3$) 14.28 (1H, s), 13.92(1H, s), 13.77(1H, bs), 7.68 (1H, dd, J = 8 and 1Hz), 7.52 (1H, t, J = 8Hz), 7.36 (5H, m), 6.95 (1H, dd, J = 8 and 1 Hz), 4.73 (2H, d, J = 6Hz), 2.96 (2H, t, J = 8Hz), 2.75 (2H, t, J = 8Hz); (Found: C, 72.2; H, 4.9; N, 3.9; m/z 347.1148. $C_{21}H_{17}NO_4$ requires C, 72.6; H, 4.9; N, 4.0%; m/z 347.1157).

Reaction of (9) with pyrrolidine gave 1,5-dihydroxyanthraquinone (10%), while hydrolysis with acid or base gave 1,4,5-trihydroxyanthraquinone (40%).

Catalytic hydrogenation of (9).- A solution of (9) (20 mg) in CH_3CO_2H (25 ml) was hydrogenated over a platinum catalyst (10 mg ex Adams PtO_2). After 24 h the mixture was filtered, diluted with water (50 ml) and extracted with CH_2Cl_2 (2 x 30 ml). The combined CH_2Cl_2 extracts were washed with H_2O (100 ml), dried (Na_2SO_4) and evaporated to give a yellow solid (12 mg) consisting of two products. T.l.c. on silica eluting with CH_2Cl_2 afforded 1,5-dihydroxyanthraquinone (3.5 mg), and a yellow solid (5 mg) m.p. 169-171°C; ν_{max} ($CHCl_3$) 3400-2740, 1640 cm^{-1}; λ_{max} ($CHCl_3$) 240(3611), 282(5555), 292(5740), 444(ε1450) nm; δ (300 MHz, CD_2Cl_2) 11.85 (2H, s), 2.85 (4H, bt); 2.64 (4H, m), 2.04 (4H, bt): (m/z 246.0893; $C_{14}H_{14}O_4$ requires 246.0892) [formulated as (10)].

Catalytic hydrogenation of 1,5-dihydroxyanthraquinone.- Hydrogenation of 1,5-dihydroxyanthraquinone (20 mg) was carried out as in the previous experiment for a period of 6 h. The usual workup afforded a yellow solid (16 mg), consisting of two yellow products and one colourless product. T.l.c. on silica eluting with CH_2Cl_2 afforded (10) (2 mg), the known quinone (11) (8 mg), m.p. 168-171°C; ν_{max} ($CHCl_3$) 2920, 2860, 1640 cm^{-1}; λ_{max} ($CHCl_3$) 265(17,062), 274(ε17,494) nm; δ (300 MHz, CD_2Cl_2) 2.31 (8H, m), 1.60 (8H, m); m/z 216.1158. $C_{14}H_{16}O_2$ requires 216.1150); and a colourless product (3 mg), m.p.153-155°C; ν_{max} ($CHCl_3$) 3660, 3450, 2900, 2860, 1600 cm^{-1}; δ (300 MHz, CD_2Cl_2) 1.84-0.9; m/z 402.2562; $C_{28}H_{34}O_2$ requires 402.2559) formulated as (12).

Piperidinium acetate catalysed alkylation of imine (8).- A suspension of the imine (8) (200 mg) in Pr^iOH (50 ml) was reacted under a nitrogen atmosphere with propanal (582 mg) and a solution of peridinium acetate (106 mg) in Pr^iOH (5 ml) and the mixture was boiled under reflux for 8 h. The solvent was evaporated to give a gummy purple solid, which was dissolved in CH_2Cl_2 (50 ml), washed with H_2O (150 ml), dried (Na_2SO_4) and evaporated to afford a solid (220 mg), consisting of the product and small amount of starting material. Chromatography on silica eluting with CH_2Cl_2 afforded, after crystallisation from $CHCl_3$/hexane, 1,5-dihydroxy-4-n-propylamino-2-propylanthraquinone as purple crystals (198 mg), m.p. 133-134°C; ν_{max} ($CHCl_3$) 3680, 2940, 2870, 1590 cm^{-1}; λ_{max} ($CHCl_3$) 240(33,686), 252(25,423), 308(6567), 392(2542), 536(9216), 570(16,101), 614(ε17,690) nm; δ (300 MHz, $CDCl_3$) 14.60(1H, s), 13.51 (1H, s), 10.06 (1H, bs), 7.89 (1H, dd, J = 8 and 1 Hz), 7.62 (1H, t, J = 8 Hz), 7.28(1H, dd, J = 8 and 1 Hz), 7.08 (1H, s), 3.39 (2H, q), 2.72 (2H, t, J = 7.5 Hz), 1.80 (2H, m), 1.72 (2H, m), 1.09 (3H, t, J = 7.5 Hz), 1.02 (3H, t, J = 7.5 Hz); (Found: C, 70.6; H, 6.2; N, 4.1; m/z 339.1463. $C_{20}H_{21}NO_4$ requires C, 70.8; H, 6.2; N, 4.1% m/z 339.1470)

Piperidinium acetate catalysed alkylation of imine (9).- The same procedure was carried out as in the previous experiment, except compound (9) (232 mg) was used instead of (8). Chromatography of the product on silica eluting with 1 : 1 EtOAc : hexane, afforded after crystallisation from $CHCl_3$ /hexane, 4-benzylamino-1,5-dihydroxy-2-propylanthraquinone (15) as dark purple crystals (194 mg), m.p. 163-165°C; ν_{max} ($CHCl_3$) 2940, 2880, 1590 cm^{-1}; λ_{max} ($CHCl_3$) 240(34,466), 252(27,184), 304(6553), 528(8737), 562(15,776), 605(ε 16,262) nm; δ(300 MHz, CD_2Cl_2) 14.42 (1H, s), 13.29 (1H, s), 10.27 (1H, bt), 7.78 (1H, dd, J = 8 and 1 Hz), 7.56 (1H, t, J = 8 Hz), 7.30 (5H, m), 7.18 (1H, dd, J = 8 and 1 Hz), 7.00 (1H, s), 4.60 (2H, d, J = 6 Hz), 2.57 (2H, t, J = 7.5 Hz), 1.52 (2H, m), 0.82 (3H, t, J = 7.5 Hz), (m/z 387.1474. $C_{24}H_{21}NO_4$ requires 387.1470).

Hydrogenolysis of 4-benzylamino-1,5-dihydroxy-2-propylanthraquinone (15).- A solution of (15) (30 mg) in CH_3CO_2H (40 ml) was hydrogenated over 5% palladium on charcoal (5 mg). After 2 h, the mixture was filtered, then diluted with H_2O (50 ml) and extracted with CH_2Cl_2 (2 x 30 ml). The combined extracts were washed with water (150 ml), dried (Na_2SO_4), passed through plug of silica and evaporated to give pure 4-amino-1,5-dihydroxy-2-propylanthraquinone (16) as a purple solid (21.4 mg), m.p. 167-170°C; ν_{max} ($CHCl_3$) 3500, 3330, 1600, 1580 cm^{-1}; λ_{max} 244(27,695), 252(23,420), 306(6319), 396(1579), 512(8178), 540(12,732), 580(ε 11,524) nm; δ (300 MHz, CD_2Cl_2) 14.32 (1H, s), 13.30 (1H, s), 7.82 (1H, dd, J = 8 and 1 Hz), 7.60 (1H, t, J = 8 Hz), 7.23 (1H, dd, J = 8 and 1 Hz),6.98 (2H, bs), 6.87 (1H, s), 2.62 (2H, t, J = 7.5 Hz), 1.64 (2H, m), 0.95 (3H, t, J = 7.5 Hz), (m/z 297.1001; $C_{17}H_{15}NO_4$ requires 297.1001).

1,5-dihydroxy-2-propylanthraquinone.- CH_3CO_2H (4 ml) was added at room temperature to a stirred mixture of (17) (30 mg) in CH_2Cl_2 (20 ml) and zinc dust under Ar. After 24 h the mixture was filtered and evaporated to give a residue which was then refluxed with 10MHCl (20 ml) for 2 h. The solution was diluted with water (50 ml) and extracted with CH_2Cl_2 (3 x 25 ml). The combined extracts were washed with water (100 ml), dried (Na_2SO_4) and evaporated to give a purple solid (24 mg). T.l.c. on silica eluting with 1 : 1 CH_2Cl_2 : hexane gave 1,5-dihydroxy-2-propylanthraquinone (18) as a yellow solid (10 mg), m.p. 131-133°C; ν_{max} ($CHCl_3$) 2915, 2870, 1625, 1600, 1580 cm^{-1}; λ_{max} ($CHCl_3$) 256(14,901), 280(6355), 290(6638), 404(4519), 426(6497), 436(ε 6567) nm; δ (300 MHz, CD_2Cl_2) 13.02 (1H, s), 12.68 (1H, s), 7.83 (1H, d, J = 8 Hz), 7.77 (1H, dd, J = 8 and 1 Hz), 7.68 (1H, t, J = 8 Hz), 7.45 (1H, dd, J = 8 and 1 Hz),7.29 (1H, d, J = 8 Hz), 2.69 (2H, t, J = 7.5 Hz), 1.63 (2H, m), 0.94 (3H, t, J = 7.5 Hz), (m/z 282.0892; $C_{17}H_{14}O_4$ requires 282.0892).

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REFERENCES

1. A. E. Ashcroft, D. T. Davies, and J. K. Sutherland, Tetrahedron, 1984, 40, 4579.
2. P.G. Marshall, J.Chem. Soc., 1937, 254.
3. L. M. Harwood, L. C. Hodgkinson, J. K. Sutherland, and P. Towers, Can.J. Chem., 1984, 62, 1922.
4. A. Kumar, unpublished work.
5. A. Skita, Chem. Ber., 1927, 60, 2552.
6. K. Kikuchi, T. Yamagishi, and M. Hida, Dyes and Pigments, 1981, 2, 143.
7. G. C. Ley and R. L. Lichter, "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy", Wiley, 1979.
8. P. N. Preston, T. Winwick, and J. O. Morley, J. Chem. Soc., Perkin Trans.1, 1983, 1439.

Footnote.

#The absorption of (10) in the visible was unexpected and since it is close to that of 1,5-dihydroxyanthraquinone we examined the solution by t.l.c. after determination of the u.v. spectrum; this showed only the presence of (10). However, there must remain some question as to whether the u.v. spectrum is an artefact or is due to an unusual chromophore.