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FORMATION OF A NITRILE VIA ZINC IODIDE - CATALYZED OPENING OF A BAY-REGION POLYCYCLIC AROMATIC HYDROCARBON EPOXIDE BY TRIMETHYLSILYL CYANIDE

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ABSTRACT

Reaction of the epoxide ring of the carcinogen (±)-7β,8α-dihydroxy-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene (1) with trimethylsilyl cyanide in the presence of ZnI_2 has been examined Protection of the hydroxyl groups of the carcinogen followed by epoxide opening provides a mixture of *trans* and *cis* 9-trimethylsilyl-10-cyano derivatives (4 and 5) The formation of nitriles was confirmed by ^{13}C NMR, IR and hydrolysis of 4 to its amide This is contrary to results reported for monocyclic and bicyclic rings

Epoxides have been reported to react with trimethylsilyl cyanide in the presence of aluminium catalysts to yield the trimethylsilyl ethers of β-hydroxy nitriles[1-3] On the other hand, opening of epoxides with use of ZnI_2 (or $ZnCl_2$) catalyst affords the trimethylsilyl ethers of β-hydroxy isonitriles[1,3-6] These can be subsequently hydrolyzed to produce stereospecifically substituted β-amino alcohols[1,3-4,6] Because of the ease and high yields of these reactions, we investigated whether this methodology could be used to introduce an amino group at the C-10 position of the carcinogen (±)-7β,8α-dihydroxy-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene (BPDE) (1) to give an intermediate for the synthesis of naturally occurring nucleoside adducts[6]

RESULTS AND DISCUSSION

Attempts to prepare 7β,8α-dihydroxy-9α-trimethylsilyloxy-10β-isocyano-7,8,9,10-tetrahydrobenzo[a]pyrene (2) from BPDE (1) by a rational synthetic route[1] failed Trimethylsilyl cyanide reacts with hydroxy compounds to give the corresponding O-trimethylsilylated compounds[7], and it is possible that the two hydroxy groups in 1 are attacked by trimethylsilyl cyanide before opening of the epoxide ring Accordingly, the reaction was repeated using a larger excess of trimethylsilyl cyanide In addition, difficulties created by the low solubility of 1 in methylene chloride were overcome by use of a methylene chloride/THF solvent mixture However, the desired isocyanide was still not obtained

Reaction of 1 with N,O-bis(trimethylsilyl)trifluoroacetamide allows protection of the hydroxyl groups[8] prior to ring opening This provided (±)-7β,8α-bis(trimethylsilyloxy)-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene (3) in quantitative yield The epoxide ring of 3 was then opened using trimethylsilyl cyanide and zinc iodide in methylene chloride This afforded a mixture of stereoisomers 4 and 5 (Scheme I) in the ratio 1 1 1 with a variable amount (1-14%) of a minor product (6) The formation of two major products and the long reaction time observed here, in contrast to the rapid production of a single *trans* product reported for other epoxides, is probably due to steric effects of the protected hydroxyl groups or the pyrene nucleus The structures of 4 and 5 were established from their spectroscopic properties

The ^{1}H NMR spectrum of 4 displayed a sharp singlet at δ 0 2 integrating to nine protons and two singlets near δ 0 31 corresponding to eighteen protons These protons were assigned to three trimethylsilyl groups, indicating that the epoxide ring underwent cleavage A doublet at δ 5 09 was attributed to H-10 because its coupling (J = 3 46 Hz) is identical to that for H-10 after addition of other nucleophiles[9] to C-10 of 1 The small coupling constant suggests that H-9 and H-10 occupy quasi-equatorial positions, which would indicate that 4 is produced by the *trans* addition of trimethylsilyl cyanide to C-10 of 3 A double doublet at δ 4 13-4 14 with coupling constants 3 41 Hz (close to that observed for H-10) and 1 59 Hz was identified as H-9 A double doublet at δ 4 69-4 70 with a weaker coupling ($J_{8a,9e}$ = 1 56 Hz) near that of H-9 was identified as H-8 The stronger coupling of H-8 (J = 6 45 Hz) matched the coupling of a doublet at δ 4 81-4 82 (J = 6 48 Hz) identifying the latter resonance as H-7 The discrepancy between the values of $J_{7,8}$ observed for this molecule and literature values for other C-10 BPDE derivatives[9] suggests that this molecule assumes a different conformation Addition of cyanide to C-9 is unlikely in light of the preference for nucleophilic attack at the benzylic C-10 position A downfield doublet at δ 8 35-8 37 (J = 9 28 Hz) was identified as H-11 on the basis of possible steric interaction of this bay region hydrogen with H-10 A doublet at δ 8 25-8 27 with coupling constant 9 30 Hz, characteristic of ortho coupling, was identified as H-12 H-3 and H-1 appeared as doublets at δ 8 18-8 19 and δ 8 22-8 24,

Scheme I

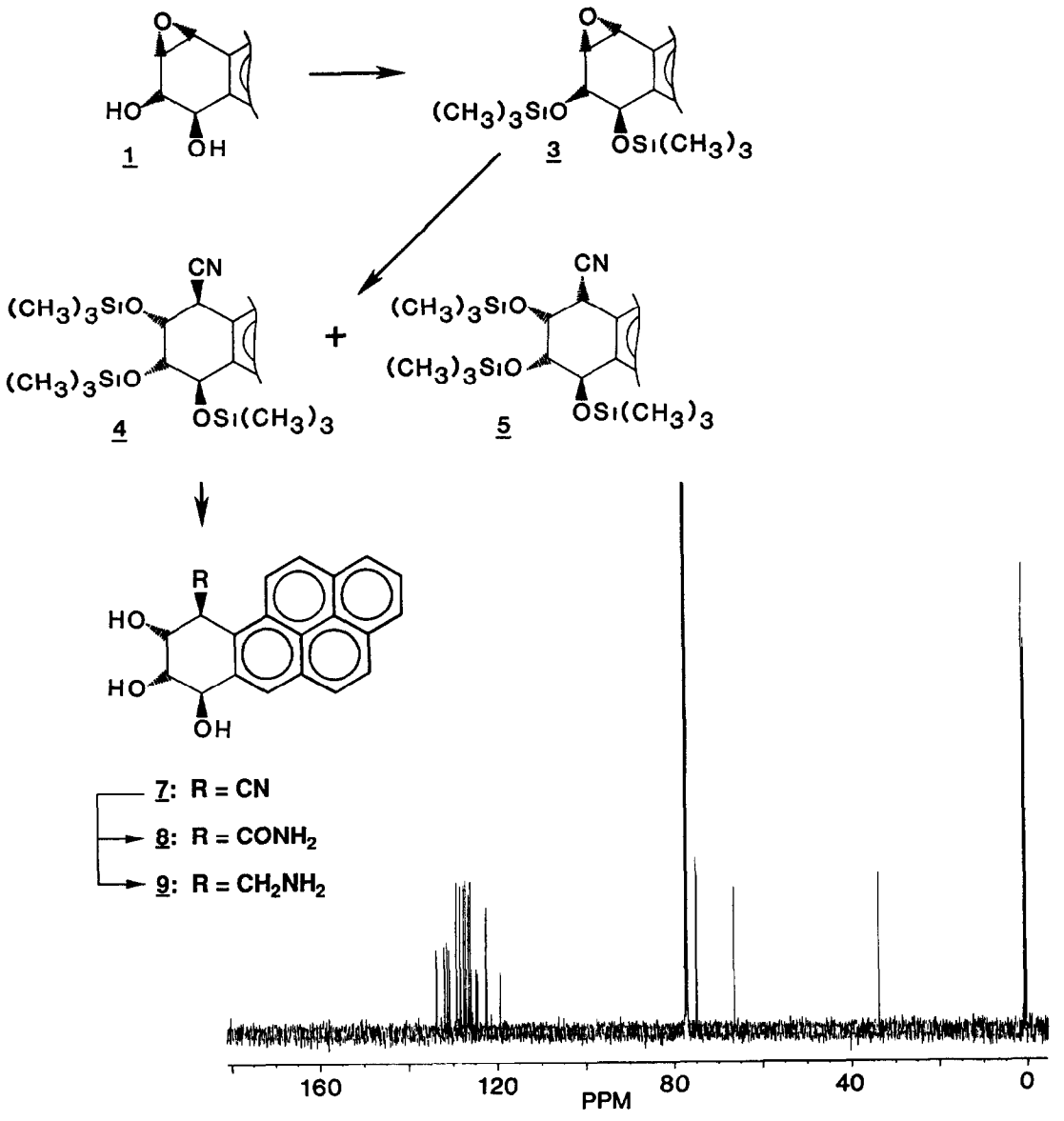

Figure 1 500 MHz ^{13}C NMR spectrum of (±)-7β,8α,9α-tris(trimethylsilyloxy)-10β-cyano-7,8,9,10-tetrahydrobenzo[a]pyrene (4) in $CDCl_3$

respectively The remaining aromatic hydrogens were a multiplet at δ 7 99-8 07 ^{13}C NMR showed three singlets at δ 0 06, 0 26 and 0 54, respectively, confirming the presence of three trimethylsilyl groups (Figure 1) Four peaks at δ 33 43, 66 21, 74 63 and 74 73 were assignable to the alicyclic carbons The upfield peak was attributed to C-10, which carries the cyano substituent The aromatic carbon peaks were observed at δ 122 25-133 47 The presence of an extra peak in the aromatic region at δ 119 16 suggested the presence of a cyano group in **4** This was supported by the absence of a low field singlet between δ 140-180 characteristic of isocyanide carbon and the lack of an isocyanide absorption in its IR The presence of a cyano group was also indicated by an IR absorption at 2260 cm^{-1} typical of C≡N stretching Hence, **4** was characterized as (±)-7β,8α,9α-tris(trimethylsilyloxy)-10β-cyano-7,8,9,10-tetrahydrobenzo[a]pyrene This was substantiated by mass spectrometry. Ionization by electron impact provided a parent ion at m/z 545 and a base peak at 73

In contrast to **4**, H-10 in **5** appeared as a doublet at δ 5 11-5 12 with a larger coupling constant $J_{9,10}$ = 5 95 Hz This indicated that **5** was obtained by *cis* addition of trimethylsilyl cyanide to disilylated BPDE (**3**) at C-10 and is in agreement with a previous report[9] H-9 appeared as a double doublet (as in **4**) at δ 4 19-4 21 ($J_{9e,10a}$ = 6 03 Hz, $J_{8a,9e}$ = 1 73 Hz) A double doublet at δ 4 86-4 87 (J = 1 70 Hz, 6 41 Hz) was assigned to H-8, and a doublet at δ 4 71-4 73 (J = 6 43 Hz) was assigned to H-7 The aromatic proton resonances were found at about the same positions as in **4** Trimethylsilyl protons appeared as three singlets at δ 0 18, 0 29 and 0 37 IR of **5** again showed absorption at 2260 cm^{-1} characteristic of C≡N stretching This data suggested that **5** was (±)-7β,8α,9α-tris(trimethylsilyloxy)-10α-cyano-7,8,9,10-tetrahydrobenzo[a]pyrene This structure was supported by high resolution mass spectrometry The IR spectrum of **6** also exhibited a cyanide band, but was not further characterized

The presence of a cyano group in **4** was confirmed by deprotection, followed by hydrolysis Treatment of **4** with potassium fluoride in methanol did not produce the desired product (**7**), contrary to expectation[1,4-6] However, **4** on treatment with citric acid in methanol[10,11] provided (±)-7β,8α,9α-trihydroxy-10β-cyano-7,8,9,10-tetrahydrobenzo[a]pyrene (**7**) in quantitative yield The disappearance of the singlet at δ 0 20 and the two singlets near δ 0 31 in the ^1H NMR spectrum of **7** indicated complete removal of the trimethylsilyl groups This was supported by observing three singlets at δ 5 38, 5 78 and 5 80 assignable to three hydroxyls which disappeared on exchanging with D_2O The large coupling (J = 6 58 Hz) associated with the doublet at δ 5 26-5 27 identified it as H-7 The H-10 resonance was observed as a singlet at δ 5 02 The unresolved doublet at δ 4 48-4 49 and a singlet at δ 4 13 were assigned to H-8 and H-9, respectively, by comparison of the chemical shifts with those of **4** The change of splitting pattern observed for H-8, H-9 and H-10 in **7** relative to **4** indicates that the ring conformation is altered Liquid SIMS exhibited a peak at m/z 329 representing the molecular ion of **7** An IR band attributable to the

nitrile function was observed at 2260 cm^{-1}, as in **4** Thus, **7** was identified as (±)-7β,8α,9α-trihydroxy-10β-cyano-7,8,9,10-tetrahydrobenzo[a]pyrene

The hydrolysis of **7** with methanolic hydrochloric acid gave **8** (Scheme I) in quantitative yield The partial or complete hydrolysis of a cyano group should lead to an amide or acid, respectively, while an isonitrile would provide formylamine or amine. The structure of **8** was determined on the basis of its ^1H NMR, mass and IR spectra. The chemical shifts of all alicyclic protons undergo significant changes compared to **7** H-8, H-9 and H-10 signals shift downfield with the smallest shift observed in H-8 (0 18 ppm), while the H-7 signal moves 0 47 ppm upfield. This data suggests a different functionality on C-10 in **8** This is confirmed by the presence of an extra peak in the benzo[a]pyrene proton region at δ 8 4 assignable to the amido function which disappears upon exchange with D_2O. The appearance of two hydroxyl signals far downfield (0 61 ppm) compared to **7** further supports the presence of a different adjacent substituent The infrared spectrum of **8** exhibited absorption bands at 1644 5 and 1757 cm^{-1} which are characteristic of amides High resolution FAB mass spectrometry exhibited a peak at M+1 (m/z 348) A base peak at m/z 330 which could arise from M+1 by loss of water further supports the structure since the formation of this fragment is more probable in **8** than from a formylamine derivative No further hydrolysis of **8** was observed after several days of refluxing in methanolic HCl Thus, **8** was identified as (±)-7β,8α,9α-trihydroxy-10β-amido-7,8,9,10-tetrahydrobenzo[a]-pyrene

Additional evidence for the structure of **4** was obtained by subjecting **7** to catalytic reduction with 10% Pd/C This gave a mixture of starting material (**7**) and a product (**9**) (Scheme I) in the ratio of 2 1 The lack of completion of the reaction may be due to steric hindrance (which may also account for the partial hydrolysis of **7** noted above) A high resolution mass spectrum of this crude reaction mixture showed a peak at m/z 333 assignable to (±)-7β,8α,9α-trihydroxy-10β-aminomethyl-7,8,9,10-tetrahydrobenzo[a]pyrene (**9**) indicating that reduction had occurred, as well as a peak at m/z 329 due to **7**

We have shown that trimethylsilyl cyanide behaves as an ambident nucleophile in its zinc-catalyzed reaction with epoxides A nitrile is formed with 7β,8α-bis(trimethylsilyloxy)-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene, in contrast to the reported formation of isonitriles with epoxides in simpler ring systems The unexpected course of this reaction may result from steric crowding in the bay region of the benzo[a]pyrene derivative

EXPERIMENTAL

Melting points (uncorrected) were taken on a Thomas Hoover capillary melting point apparatus IR spectra were recorded on Perkin Elmer 283 spectrophotometer UV spectra were obtained on a Hewlett-Packard 8450A spectrophotometer MS was performed on a Kratos MS 50 spectrometer ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker 500 MHz spectrometer

Elemental analyses were performed by the microanalytical laboratory, University of California, Berkeley.

(±)-7β,8α-Bis(trimethylsilyloxy)-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene (3)

N,O-bis(trimethylsilyl)-trifluoroacetamide (80 mL) was added to a stirred solution of benzo[a]pyrene diol epoxide (**1**) (1 01 g, 3 34 mmol) in dimethylformamide (50 mL) After 3 h of stirring at room temperature under nitrogen, the solvent and excess of silylating reagent were removed by rotary evaporation to afford **3** as a pale yellow solid Recrystallization from methylene chloride yielded white crystalline solid (1 47 g, 100%) The spectral data for **3** (UV, IR and ^{1}H NMR) will be reported elsewhere

(±)-7β,8α,9α-Tris(trimethylsilyloxy)-10β-cyano-7,8,9,10-tetrahydrobenzo[a]pyrene (4)
and **(±)-7β,8α,9α-tris(trimethylsilyloxy)-10α-cyano-7,8,9,10-tetrahydrobenzo[a]pyrene (5)**

Trimethylsilyl cyanide (3 0 mL, 22 5 mmol), anhydrous zinc iodide (50 mg, 0.16 mmol) and dry methylene chloride (3 2 mL) were added to a three-necked flask equipped with water condenser, nitrogen inlet, magnetic stirrer and dropping funnel The mixture was stirred and heated to reflux at 42-3 °C in an oil bath and then a solution of **3** (1 04 g, 2 33 mmol) in dry methylene chloride (10 mL) was added in portions over a period of 1 h After refluxing 4 days, TLC (C_6H_6 and 50% C_6H_6/hexane) showed no further increase in products and the mixture was evaporated The crude isomeric products were dissolved in methylene chloride, washed with water (2x10 mL), dried ($MgSO_4$) and filtered Evaporation yielded a yellow solid which was purified by flash chromatography (silica gel, 40% C_6H_6/hexane) to afford **4** (400 mg), **5** (450 mg) and **6** (6 mg)

4 R_f 0 43 (benzene), mp 204-6 °C, IR (KBr) 3060, 2970, 2920, 2260, 1610, 1450, 1380, 1350, 1260, 1168, 1125, 1100, 1070, 1010, 960, 915, 845 , 760 cm^{-1}, UV (THF) 203 nm (log ε 4 88), 227(4 95), 234(4 94), 247(4 76), 280(4 87), 283(4 85), 314(3 94), 329(4 24), 345(4 42), 378(3 23), mass spectrum (EI), m/z (relative intensity) 545(M^+, 26 76), 455(16 08), 367(23 20), 341(83 31), 313(15 08), 265(19 12), 242(74 96), 214(51 84), 191(75 50), 147(57 89), 103(13 34), 73(100), ^{1}H NMR ($CDCl_3$) δ 0 20 (s, 9, $(CH_3)_3Si$), 0 308 (s, 9, $(CH_3)_3Si$), 0 313 (s, 9, $(CH_3)_3Si$), 4 13-4 14 (dd, 1, H-9, $J_{9e,10e}$ = 3 41 Hz, $J_{8a,9e}$ = 1 59 Hz), 4 69-4 70 (dd, 1, H-8, $J_{7a,8a}$ = 6 45 Hz, $J_{8a,9e}$ = 1 56 Hz), 4 81-4 82 (d, 1, H-7, $J_{7a,8a}$ = 6 48 Hz), 5 09 (d, 1, H-10, $J_{9e,10e}$ = 3 46 Hz), 7 99-8 07 (m, 4, aro H), 8 18-8 19 (d, 1, H-3, J = 7 39 Hz), 8 22-8 24 (d, 1, H-1, J = 7 79 Hz), 8 25-8 27 (d, 1, H-12, $J_{11,12}$ = 9 30 Hz), 8 35-8 37 (d, 1, H-11, $J_{11,12}$ = 9 28 Hz), ^{13}C NMR($CDCl_3$) δ 0 06 ($(CH_3)_3Si$), 0 26 ($(CH_3)_3Si$), 0 54 ($(CH_3)_3Si$), 33 43 (C-10), 66 21, 74 63, 74 73, 119 16, 122 25, 122 32, 124 32, 124 62, 125 77, 125 85, 126 28, 126 94, 127 37, 128 14, 128 99, 129 07, 130 61, 131 11, 131 72, 133 47
Anal Calcd for $C_{30}H_{39}NO_3Si_3$ C, 66 06, H, 7 16, N, 2 57 Found C, 66 20, H, 7 29, N, 2 43

5 R_f 0 51 (benzene); mp 145-7 °C, IR(KBr) 3060, 2970, 2920, 2260, 1610, 1450, 1410, 1372, 1260, 1150, 1100, 980, 900, 845, 760, 720 cm^{-1}, UV(THF) 207 nm (log ε 4 60), 247(4 69), 268(4 43), 279(4 57), 302(3 73), 315(4 09), 329(4 46), 345(4 57), 366(3 33), 378(3 11), 387(3 17), ^{1}H NMR ($CDCl_3$) δ 0 18 (s, 9, $(CH_3)_3Si$), 0 29 (s, 9, $(CH_3)_3$ Si), 0 37 (s, 9, $(CH_3)_3Si$), 4 19-4 21 (dd, 1, H-9, $J_{9a,10e}$ = 6 03 Hz, $J_{8e,9a}$ = 1 73 Hz), 4 71-4 73 (d, 1, H-7, $J_{7e,8e}$ = 6 43 Hz), 4 86-4 87 (dd, 1, H-8,

$J_{8e,9a}$ = 1 70 Hz, $J_{7e,8e}$ = 6.41 Hz), 5 11-5 12 (d, 1, H-10, $J_{9a,10e}$ = 5.95 Hz), 8 00-8.07 (m, 4, aro.H), 8 14 (s, 1, H-6), 8.18-8.22 (d, 1, H-12, J = 9 8 Hz), 8 23-8.25 (t, 1, H-2), 8 38-8 39 (d, 1, H-11, $J_{11,12}$ = 9 29 Hz).
Anal Calcd for $C_{30}H_{39}NO_3Si_3$ C, 66 06, H, 7 16; N, 2 57 Found C, 66 54, H, 6 96, N, 2 09

6 R_f 0 12 (benzene), mp 166-75 °C, IR(KBr) 3060, 2970, 2940, 2920, 2865, 2260, 1720(br), 1610, 1490, 1445, 1410, 1380, 1260, 1180, 1150, 1125, 1095, 1035, 990, 950, 905, 845, 760, 695 cm^{-1}, UV(THF) 246 nm (log ε 4 67), 268(4.43), 279(4 58), 302(3 78), 315(4 09), 329(4 44), 345(4 57), 366(3 63), 387(3 37), 393(3 19); ^1H NMR ($CDCl_3$) δ 0 15-0.41 (m, 27, three $(CH_3)_3Si$), 4 24-4 27 (d, 1H), 4 41-4 45 (d, 1H), 5.20-5.24 (t, 1H), 5 58-5 67 (d, 1H), 7 79-8 50 (m, 8, aro H).

(±)-7β,8α,9α-Trihydroxy-10β-cyano-7,8,9,10-tetrahydrobenzo[a]pyrene (7)

Citric acid (55 mg, 0 29 mmol) was added to a stirred solution of 4 (50 mg, 0 092 mmol) in methanol (10 mL) Stirring was continued at room temperature under nitrogen and the reaction monitored by TLC [$CHCl_3$·MeOH (9 1), blue fluorescence on exposure to UV light] Crystals of 7 began to appear after 5 3 h, at 7 3 h TLC [R_f (4) 0 86, R_f (7) 0 24, $CHCl_3$ MeOH (9 1)] showed the reaction was complete The suspension was filtered to give 7 (11 2 mg) as a white crystalline solid The filtrate was evaporated and the residue washed with 1% sodium bicarbonate solution (2x15 mL) and water (2x10 mL) Recrystallization of the residue from methanol yielded additional 7 (18 mg) as white crystals: mp 216-218 °C; IR(KBr) 3440, 3300, 3060, 2940, 2260, 1605, 1030 cm^{-1}, UV(DMSO) 268 nm (log ε 4 39), 279 5(4 63), 315 5(4 06), 329 5(4 44), 346(4 61), ^1H NMR(DMSO-d_6) δ 4 13 (s, 1, H-9), 4.48-4 49 (d, 1, H-8), 5 02 (s, 1, H-10), 5 26-5 27 (d, 1, H-7, $J_{7a,8a}$ = 6 58 Hz), 5 38 (s, 1, OH, exchanges with D_2O), 5 78 (s, 1, OH, exchanges with D_2O), 5 80 (s, 1, OH, exchanges with D_2O), 8 10-8 13 (t, 1, H-2), 8 19-8 20 (d, 2, H-1, H-3), 8.32-8 34 (d, 2, H-4, H-5, $J_{4,5}$ = 9 86 Hz), 8 37 (s, 1, H-6), 8 38-8 40 (d, 1, H-12, $J_{11,12}$ = 9 02 Hz), 8 43-8 45 (d, 1, H-11, $J_{11,12}$ = 9 37 Hz)
Anal Calcd for $C_{21}H_{15}NO_3$: C, 76 60, H, 4 56, N, 4 26 Found C, 76 17, H, 4 59, N, 4 02

(±)-7β,8α,9α-Trihydroxy-10β-amido-7,8,9,10-tetrahydrobenzo[a]pyrene (8)

7 (15 mg, 0 046 mmol) was dissolved in hot methanol (8 mL) After cooling, conc HCl (270 uL) was added; the mixture was then stirred at 65 °C under nitrogen overnight The precipitate was filtered and dried to give 8 (15 mg, 94 8%) as a white solid R_f 0 46 ($CHCl_3$ MeOH [9 1]), mp 286-9 °C dec , IR (KBr) 3465 6-3261 7 (br), 3121 1, 3078 9, 3029 7, 2938 3, 1799 2, 1757, 1644 5, 1609 4, 1349 2, 1321 1, 1250 8, 1222 6, 1159.4, 1103 1, 1060 9, 1032 8, 1011 7, 983 59, 885 16, 850, 835 94, 751 56, 730 47, 702.34, 540 62 cm^{-1} , mass spectrum (FAB), m/z 348 $(M+1)^+$, 330, 314, 285, 269, 257, 239, ^1H NMR ($CDCl_3$) 4 66-4 67 (d, 1H), 4 70 (s, 1H), 4 79-4 80 (d, 1H), 5 23-5 24 (d, 1, OH, J=3 2 Hz, exchanges with D_2O), 5 24-5 25 (d, 1, H-10, J=3 26 Hz), 6 23-6 24 (d, 1, OH, J=2 88 Hz, exchanges with D_2O), 6 41-6 42 (d, 1, OH, J=6 52 Hz, exchanges with D_2O), 8 09-8 13 (t, 1, H-2, J=7 68 and 7 64 Hz), 8 19-8 20 (d, 3, aro H), 8 32-8 37 (m, 3, aro H), 8 4 (s, 2, -$CONH_2$, exchanges with D_2O), 8 57-8 59 (d, 1, H-11, J=9 49 Hz)

(±)-7β,8α,9α-Trihydroxy-10β-aminomethyl-7,8,9,10-tetrahydrobenzo[a]pyrene (9)

Conc HCl (3 1 uL) was added to a stirred solution of 7 (10 mg, 0 030 mmol) in ethanol (10 mL) at 0 °C The solution was brought to room temperature and 10% Pd/C (2 5 mg) was added

After 6 h of stirring under hydrogen, the mixture was filtered and evaporated, yielding a mixture of starting material (7) (R_f = 0.37, 10% MeOH:$CHCl_3$) and 9 (R_f = 0 29), mass spectrum (FAB), m/z 334 $(M+H)^+$, 333 (M^+), 330 $(M+H)^+$, 329 (M^+), 313, 312, 299, 285, 279, 269, 257, 240, 215, 201.

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