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1,2-DIHYDROISOQUINOLINES—XII[1]
THE REACTION WITH *O*-NITROBENZALDEHYDES

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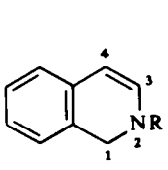
Abstract—The reaction between 1,2-dihydroisoquinolines and *o*-nitrobenzaldehydes has been shown to produce, in low yields, 4-[3-anthranilyl]isoquinolines. A new synthesis of 7*H*-dibenz[*de*,*g*]isoquinoline derivatives is also described.

IN PART X of this series[2] we described our results in the study of the interaction of 1,2-dihydroisoquinolines (**1**, R = H or Me) with a variety of aldehydes to form 4-substituted isoquinolinium salts of the type **2** (R = H or Me). The enamine was prepared either by reduction of isoquinoline salts with LAH, or by the cyclization of benzylaminoacetaldehyde acetals (**3**). We mentioned that some anomolous results had been obtained when *o*-nitrobenzaldehydes were used, and we now wish to report on these reactions.



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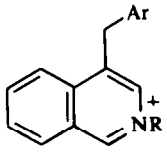

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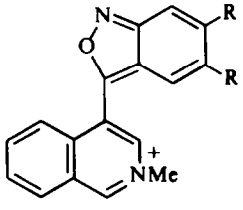

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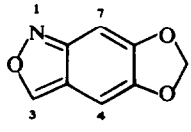

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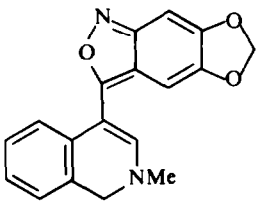
When 2-methyl-1,2-dihydroisoquinoline (**1**, R = Me) was reacted with 6-nitropiperonal in the presence of 6N HCl under the conditions described previously,[2] a 22% yield of a quaternary salt was isolated, which analysed for $C_{18}H_{13}N_2O_3Cl$; the expected product, **2** (R = Me, Ar = 2-nitro-4,5-methylenedioxyphenyl), has a molecular formula of $C_{18}H_{15}N_2O_4Cl$. The band at about 1510 cm^{-1} in the IR spectrum expected for the nitro group was absent. The NMR spectrum (Fig. 1), measured in CF_3CO_2H solution, exhibited one proton singlets at 9·3 ppm and 8·5 ppm, downfield from internal TMS, typical of the C_1 and C_3 H atoms of an isoquino-

linium salt. A two proton singlet at 6·0 ppm and a three proton singlet at 4·6 ppm were readily assigned to the methylenedioxy and $\geq N^+$—Me groups respectively. The absorption expected at about 4·2 ppm for a methylene group at C_4 in structure **2** (R = Me) was absent and, although the total number of aromatic protons required for this structure were present, two one proton singlets at 6·6 ppm and 6·8 ppm were at rather higher field than expected. It is well known that *o*-nitrobenzaldehydes and *o*-nitroacetophenones are easily reduced to anthranils, and structure **4** (R,R = CH_2O_2) for the enamine reaction product was an obvious choice. The protons at C_4 and C_7 of 5,6-methylenedioxyanthranil (**5**) absorb at 6·8 ppm.

Anthranils typically form complexes with $HgCl_2$, and compound **4** (R,R = CH_2O_2) behaves similarly; a complex is also formed with $SnCl_2$. As expected,[4] sodium borohydride reduces **4** (R,R = CH_2O_2) to the 1,2-dihydroisoquinoline (**6**), whose structure follows from analytical and spectral data. The NMR spectrum is reproduced as Fig. II. 2-Methyl-4-(*o*-nitrobenzoyl)-1,2-dihydroisoquinoline **7** (R = NO_2, R′ = R″ = H),



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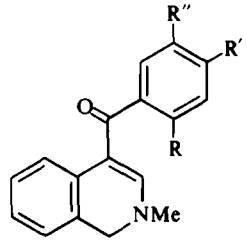

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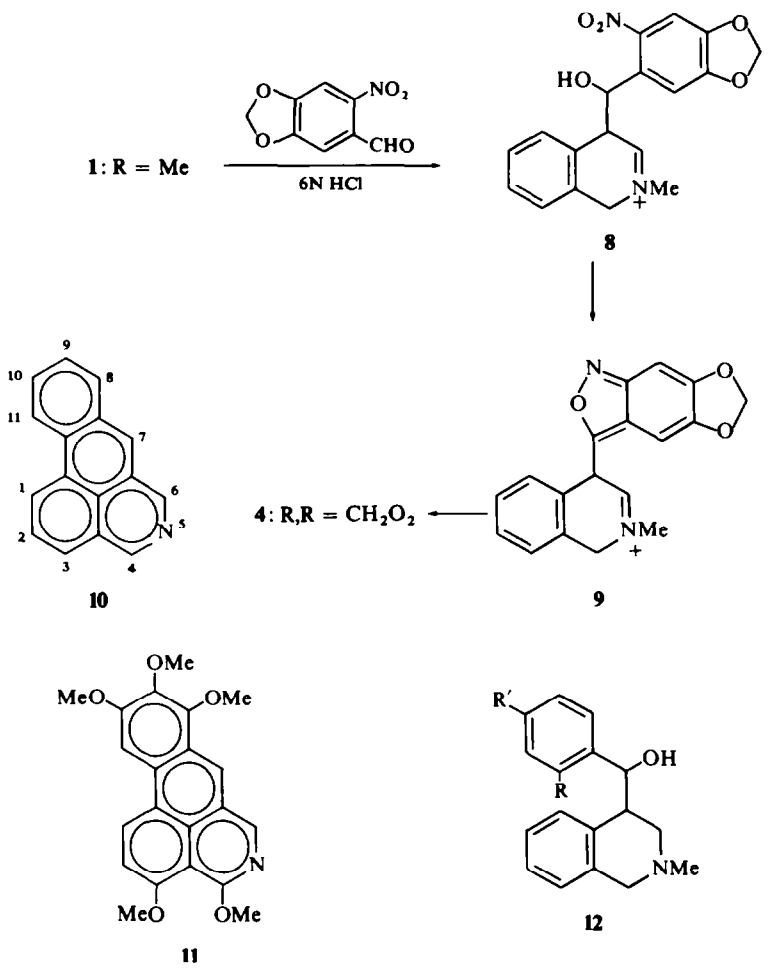
obtained[5,6] by the acylation of **1** (R = Me), has been reduced with $SnCl_2$/HCl to a compound whose analytical and spectral characteristics are in accord with the $SnCl_2$ complex of the anthranil **4** (R = H). A direct correlation between this product and the substance formed from **1** (R = Me) and *o*-nitrobenzaldehyde is, unfortunately, not possible since the latter gave the expected enamine product **2** (R = Me, Ar = *o*-nitrophenyl).

Analogous anthranil structures were produced when *o*-nitrobenzaldehyde, 6-nitropiperonal and 6-nitroveratraldehyde were reacted with some benzylaminoacetals of the type **3** under the conditions[2] which had been used previously for the formation of 4-benzylisoquinoline derivatives. These results are collected into Tables 1 and 1A.

Several mechanisms are possible for the formation of these 4-[3-anthranilyl]-isoquinolines. 1,2-Dihydroisoquinolines are known to be reducing agents, and it is possible that an anthranil is first formed which then reacts further with more 1,2-dihydroisoquinoline. However, when the anthranil **5** was reacted with **1** (R = Me) under the conditions of the original condensation, only black tars were formed. An alternative mechanism involves the condensation of the aldehyde with the 1,2-dihydroisoquinoline in the usual way[7] to form **8**, which is then further reduced by excess enamine; *o*-nitrobenzylalcohols are known[3] to yield anthranils on reduction. A possible sequence of events is shown in **1** (R = Me) → **9** → **4** (R,R = CH_2O_2).

One of our original reasons for attempting the preparation of 4-(*o*-nitrobenzyl)-



isoquinolines was the intention to develop new routes to the little studied dibenz[*de*,*g*] isoquinoline system **10**. The first synthesis in this series was achieved by Pschorr,[8] and the derivative **11** has also been described.[9] We have attained our objective by carrying out a Pschorr ring-closure on **12** (R = NH_2, R′ = H), thus forming the tetracyclic compound **13**; subsequent dehydration yielded **14**. The structure **14** has been confirmed by an alternative synthesis from the anhydride[8] **15** (Z = 0); treatment of this material with methylamine yielded **15** (Z = NMe), which, on reduc-

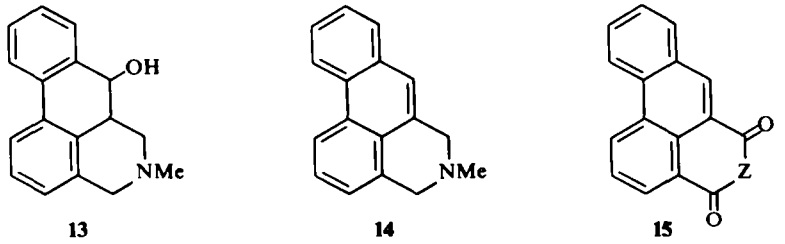


TABLE 1. SPECTRA OF 4(3′-ANTHRANILYL)-ISOQUINOLINIUM CHLORIDES

Substitution pattern	UV (Ethanol)	IR (Nujol)	NMR (CF_3CO_2H)							
	λ_{max} (ε) nm	ν_{max} cm^{-1}	C_1—H	C_3—H	C_8—H	C_6—H	C_5—H	C_4—H, C_7—H	—OCH_2O—	—OCH_3
6,7,5′,6′-Tetramethoxy-	253 (32,880), 320 (16,850)	1615	9·1	8·4	7·5		7·5	6·7, 6·8		4·0
6,7-Dimethoxy-5′,6′-methylenedioxy	252 (31,650), 320 (15,680)	1620	9·0	8·4	7·8		7·8	6·7	5·9	4·0
7,8-Dimethoxy-5′,6′-methylenedioxy-	260 (27,500), 310 (12,330)	1660, 1620	9·9	8·7		8·2	8·2	6·8, 7·0	6·1	4·3
7-Methoxy-8-hydroxy-5′,6′-methylenedioxy-	233 (33,220), 350 (16,120)	3400, 1620	9·5	8·3		7·8	7·8	6·6, 6·7	5·9	4·1
6,7-Dimethoxy-	247 (24,600), 312 (12,700)	1620	8·8	8·6	Broad absorption ~7·6 [6]					

TABLE 1A. ANALYTICAL DATA OF 4-(3′-ANTHRANILYL)-ISOQUINOLINIUM CHLORIDES

Substitution pattern	m.p. (EtOH)	% yield	Analytical results								
			Found					Requires			
			C	H	N	Cl	Mol Formula	C	H	N	Cl
6,7,5′,6′-Tetramethoxy-	218–219° (yellow needles)	10	59·2	4·9	6·6	8·3	$C_{20}H_{19}N_2O_5Cl$	59·5	4·7	6·9	8·8
6,7-Dimethoxy-5′,6′-methylenedioxy-	222–223° (pale yellow prisms)	18	59·0	4·2	7·0	9·4	$C_{19}H_{15}N_2O_5Cl$	59·0	3·9	7·25	9·2
7,8-Dimethoxy-5′,6′-methylenedioxy-	255–257° (yellow prisms)	13	59·1	4·2	7·1	9·0	$C_{19}H_{15}N_2O_5Cl$	59·0	3·9	7·25	9·2
7-Methoxy-8-hydroxy-5′,6′-methylenedioxy-	255–257° (bright yellow needles)	26	57·5	3·7	7·1	9·0	$C_{18}H_{13}N_2O_5Cl$	57·65	3·5	7·5	9·5
6,7-Dimethoxy-	216–218° (yellow prisms)	9	61·4	4·2	7·7	10·1	$C_{17}H_{15}N_2O_3Cl$	61·0	4·5	8·3	9·5

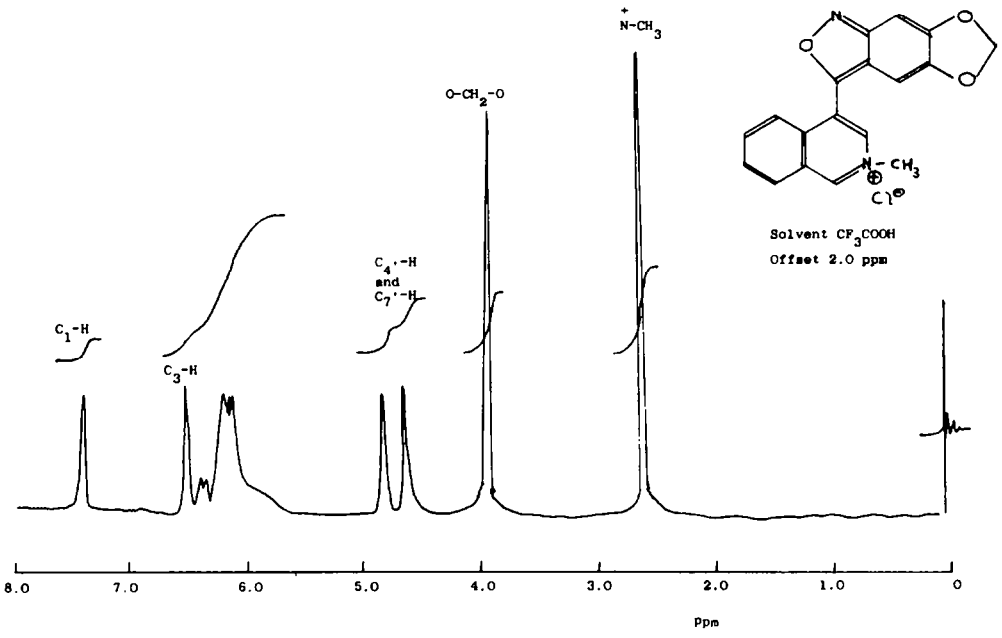
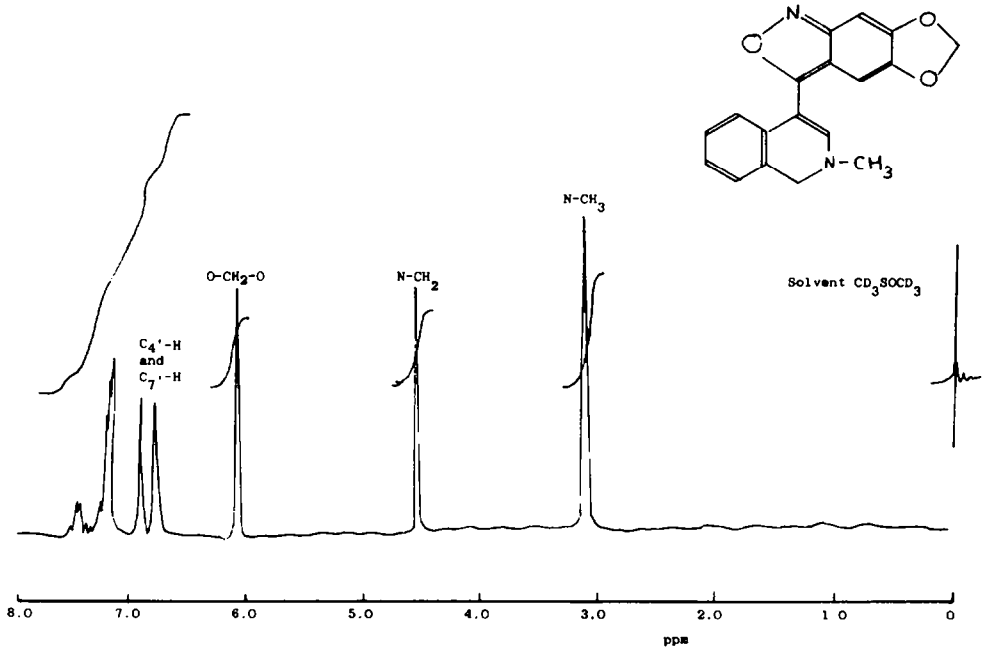

+
N-CH3
O-CH2-O
C1-H
C3-H
C4'-H
and
C7'-H
N-CH3
Cl⊖
Solvent CF3COOH
Offset 2.0 ppm
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
Ppm

FIG. 1


N-CH3
N-CH3
O-CH2-O
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C4'-H
and
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8.0
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ppm

FIG. 2

tion with LAH gave a product, identical (mixed m.p., superimposable IR spectra) with the compound obtained above. The required starting material **12** (R = NH_2, R′ = H) was easily obtained by first reducing **7** (R = NO_2, R′ = R″ = H) to **12** (R = NO_2, R′ = H) with $NaBH_4$, followed by further reduction with LAH.

We are now developing the synthesis of 7*H*-dibenz[*de,g*]isoquinolines, when we hope to examine their chemical, spectral and biological properties.

EXPERIMENTAL

5,6-*Methylenedioxyanthranil* (**5**) 6-Nitropiperonal (10 g) was added portionwise to a soln of $SnCl_2$ (30 g) in concd HCl (75 ml) at 0°. After 2 hr the product was collected by filtration, yield 7·g (84%), m.p. 110–112°: λ_{max} (ε) nm, 310 (1,410): ν_{max} cm^{-1}, 1640 (>C=N—), 1600 (>C=C<), 1200 (—O CH_2 O—); NMR (CD_3SOCD_3) ppm, 9·3 s [1](C_3—H), 6·9 s [1] and 6·7 s [1] (C_4—H and C_7—H), 6·0 s [2] (—O CH_2 O—). Formation of mercuric chloride complex was achieved by the addition of mercuric chloride (0·3 g) in EtOH (60 ml) to a soln of the anthranil (0·5 g) in EtOH (30 ml). The solid product recrystallized from EtOH as red needles (0·45 g), m.p. 231–233°, λ_{max} (ε) nm, 310 (4,850) ν_{max} cm^{-1}, 1660 (>C=N^+<), 1610 (>C=C<). NMR (DCl) ppm 9·8 s [1] (C_3—H), 7·5 s [1] and 7·4 s [1] (C_4—H and C_7—H), 6·7 s [2] (—O CH_2 O—). [[Found: C, 21·6; H, 1·4; N, 3·1; Cl, 15·8 $C_8H_5NO_3Cl_2Hg$ requires: C, 22·0; H, 1·1; N, 3·2; Cl, 16·3%].

General preparation of 4-(3′-*anthranilyl*)*isoquinolinium chlorides.* The appropriately substituted benzylaminoacetaldehyde dimethyl acetal (5 g) was heated under reflux with the *o*-nitrobenzaldehyde (molar equiv), EtOH (50 ml) and conc HCl (25 ml); the soln being protected by an atmosphere of N_2. After 30 min, the soln was allowed to cool, when the product anthranil separated. Recrystallization was achieved from EtOH in each case.

4-(5′,6′-*Methylenedioxy*-3′-*anthranilyl*)2-*methylisoquinolinium chloride*, (**4**), 2-Methyl-1,2-dihydroisoquinoline (5·5 g) in ether was added to 6-nitropiperonal (6·7 g) in EtOH (80 ml) and conc HCl (25 ml). After heating, at reflux under N_2 for 4 hrs, the soln was evaporated to small bulk, and cooled. The yellow crystals of product which separated were collected and recrystallized from EtOH, yield 3·1 g (22%), m.p. 246–248°: λ_{max} (ε) nm 240 (10,600): ν_{max} cm^{-1}, 1660 (>C=N^+<), 1640 (>C=N—), 1600 (>C=C<), 1240 (—O CH_2 O—); NMR (CF_3CO_2H) ppm, 9·3 s [1] (C_1—H), 8·5 s [1] (C_3—H), ~ 8·0 m [4] (aromatic protons), 6·7 broad s [2] (C_4—H, C_7—H), 6·0 s [2] (—O CH_2 O—), 4·6 s [3] (>N^+—CH_3). [Found: C, 63·0; H, 3·8; N, 7·8; Cl, 10·9 $C_{18}H_{13}N_2O_3Cl$ requires: C, 63·2; H, 3·8; N, 8·2; Cl 10·5%].

This compound was characterized as the mercuric chloride complex, the yellow product being recrystallized from EtOH m.p. 242–244°. [Found: C, 35·5; H, 2·0; N, 4·8; Cl, 17·0 $C_{18}H_{13}N_2O_3Cl_3Hg$ requires: C, 35·3; H, 2·1; N, 4·6; Cl, 17·3%].

4-(5′,6′-*Methylenedioxy*-3′-*anthranilyl*) 2-*methyl*-1,2-*dihydroisoquinoline*, (**6**). The anthranil (0·8 g) in EtOH (50 ml) was treated with a two molar amount of $NaBH_4$ (2 g) and the soln heated under reflux for 2 hrs. Water was then added and the mixture extracted several times with $CHCl_3$. Removal of the solvent from the combined extracts afforded crude **6**, which was recrystallized from EtOH as pale yellow prisms 0·7 g (96%), m.p. 190–192°; λ_{max} (ε) nm, 240 (18,000): ν_{max} cm^{-1}, 1655 (>C=C<), 1620 (>C=N—), 1610 (>C=C<), 1200 (—O CH_2 O—); NMR (CD_3SOCD_3) ppm, 7·4–7·1 complex [5] (aromatic protons); 6·9 s [1] and 6·8 s [1] (C_4—H and C_7—H); 6·1 s [2] (—O CH_2 O—); 3·0 s [3] (>N—CH_3). [Found: C, 70·5; H, 4·7; N, 9·2 $C_{18}H_{14}N_2O_3$ requires: C, 70·6; H, 4·6; N, 9·1%], MW (mass spec) obs. 306, calc. 306.

Treatment of 4-(3′-*anthranilyl*) *isoquinolinium chlorides with sodium borohydride.* Reaction of the salts with this reagent gave only the corresponding free bases, whose physical and analytical properties are listed below:

4-(5′,6′-*Dimethoxy*-3′-*anthranilyl*) 6,7-*dimethoxyisoquinoline*, m.p. 241–242° (EtOH), λ_{max} (ε) nm, 225 (29,860), 350 (11,200): ν_{max} cm^{-1}, 1630 (>C=N—), 1600 (>C=C<); NMR ($CDCl_3$) ppm, 9·0 s [1] (C_1—H); 8·7 s [1] (C_3—H); 7·3 s [1] and 7·5 s [1] (C_5—H and C_8—H); 6·7 s [1] and 6·8 s [1] (C_4—H

and C_7—H); 4·0 broad s [12] (—O CH_3). [Found: C, 65·2; H, 4·9; N, 7·3 $C_{20}H_{18}N_2O_5$ requires: C, 65·6; H, 4·95; N, 7·65%.]

4-(5',6'-Methylenedioxy-3'-anthranilyl) 7,8-dimethoxyisoquinoline m.p. 267–269°, λ_{max} (ε) nm, 246 (40,000): ν_{max} cm^{-1}, 1620 (>C=N—), 1615 (>C=C<); NMR (CF_3CO_2H) ppm, as for parent salt. [Found: C, 65·2; H, 3·9; N, 8·1 $C_{19}H_{14}N_2O_5$ requires: C, 65·2; H, 4·0; N, 8·0%.]

Reduction of 4-(2-nitrobenzoyl) 2-methyl-1,2-dihydroisoquinoline

(a) *The benzoyldihydroisoquinoline* (1 g) was reacted with warm $SnCl_2$ aq (5 g) in conc HCl (20 ml). After 2 hr at 100° the soln was allowed to cool and the deep orange ppt of 4-(-3'-anthranilyl) 2-methylisoquinolinium chloride–stannous chloride complex which separated was then collected, and recrystallized from DMSO, yield 35% as yellow plates, m.p. 275–277°; λ_{max} (ε) nm, 223 (35,000): ν_{max} cm^{-1}, 1660 (>C=N$^+$<), 1610, 1600 (>C=C<); NMR (CD_3SOCD_3) ppm, 9·6 s [1] (C_1—H); 8·5–7·0 complex [9] (aromatic protons); 4·4 s [3] (>N$^+$—CH_3). [Found: C, 42·2; H, 2·9; N, 6·0; Cl, 22·2 $C_{17}H_{13}N_2OCl$ requires: C, 41·9; H, 2·7; N, 5·8; Cl, 21·8%].

(b) The benzoyldihydroisoquinoline was reduced by heating in aqueous EtOH soln with excess $NaBH_4$. After 2 hr the soln was cooled, diluted with water and extracted several times with $CHCl_3$. Removal of the solvent from the combined extracts afforded 12 (R = NO_2, R = H) as colourless prisms which was recrystallized from EtOH, yield 23% m.p. 187–189°, λ_{max} (ε) nm, 265 (6,000): ν_{max} cm^{-1}, ~3500 (—OH), 1610 (>C=C<), 1520 (—NO_2); NMR ($CDCl_3$) ppm, 7·9 m [1] (aromatic proton adjacent to —NO_2 group); 7·5–6·9 m [7] (aromatic protons); 5·8 broad s [2] (—OH and —CHAr); 4·2–2·6 complex [5] (aliphatic protons); 2·5 s [3] (N—CH_3). [Found C, 68·2; H, 6·1; N, 9·2 $C_{17}H_{18}N_2O_3$ requires: C, 68·4; H, 6·1; N, 9·4%]. Acetate derivative: colourless needles m.p. 89–91° (EtOH). [Found: C, 67·3; H, 6·1; N, 8·1 $C_{19}H_{20}N_2O_4$ requires: C, 67·1; H, 5·9; N, 8·2%.]

The above tetrahydro alcohol (3 g) in dry ether (100 ml) was treated with small portions of LAH (total 3 g). After stirring at room temp for 4 hr, the excess reagent was destroyed by the cautious addition of 30% sodium potassium tartrate soln. After filtration the ethereal soln was evaporated to yield 12 (R = NH_2, R' = H) as a red oil (2·3 g). This compound was not purified but used directly in subsequent experiments.

In a similar experiment to (b) above, 7[6] (R = R'' = H, R' = NO_2) gave 30% of 12 (R = H, R' = NO_2) m.p. 197–199° (EtOH); λ_{max} (ε) nm 280 (9,200): ν_{max} cm^{-1}, 3200 (—OH) 1600 (>C=C<), 1510 (—NO_2); NMR ($CDCl_3$) ppm, 8·2–7·1 complex [8] (aromatic protons); 5·8 broad s [1] (—CH—Ar); 5·4 broad s [1] (—OH, removed by deuteration); 4·2–3·3 q [2], J = 15 H_z (Ar—C(H)(H)—N); 3·5–2·7 complex [3] (N—CH_2—CH—); 2·55 s [3] (N—CH_3). [Found: C, 68·4; H, 5·9; N, 9·2 $C_{17}H_{18}N_2O_3$ requires: C, 68·4: H, 6·1; N, 9·4%].

This compound was characterized as the O-acetate by heating with Ac_2O for 30 min at 100°, yield 76%, colourless prisms m.p. 137–139° (EtOH); λ_{max} (ε) nm 272 (7,200): ν_{max} cm^{-1}, 1725 (CH_3CO_2—), 1600 (>C=C<), 1250 (CH_3CO_2—); NMR ($CDCl_3$) ppm, 8·3–7·1 m [8] (aromatic protons); 6·2 broad s [1] (—CH—Ar) 4·1–3·0 q [2], J = 15 H_z (Ar—C(H)(H)—N); 3·0–2·4 m [3] (>N—CH_2—CH—), 2·3 s [3] (>N—CH_3); 2·0 s [3] (CH_3—CO_2—). [Found: C, 66·9; H, 5·9; N, 8·1 $C_{19}H_{20}N_2O_4$ requires: C, 67·1; H, 5·9; N, 8·2%.]

Pschorr ring closure of 12 (R = NH_2, R' = H). The amine (2·3 g) was dissolved in 2N HCl (140 ml) and diazotized at 0° by the addition of $NaNO_2$ (0·6 g) in ice cold water (50 ml). After 1 hr at 0°, urea (0·2 g) was added followed by Cu powder (2 g). At the end of a further 3 hr the suspension was filtered, basified with NaOH aq and extracted with $CHCl_3$ (3 × 30 ml). The combined extracts were dried and evaporated to give 13 as a brown gum, which crystallized on trituration with $CHCl_3$ as colourless needles (0·55 g), m.p.

176–177° ($CHCl_3$); λ_{max} (ε) nm, 273 (5,000); ν_{max} cm^{-1}, 1610, 1590 (>C=C<), 3300 (—OH); NMR (CD_3SOCD_3) ppm, 7·9–7·0 m [7] (aromatic protons); 4·5 broad s [1] (HO—C(Ar)—H); 3·9–2·7 m [5] (—CH_2—N—CH_2—, C_4—H); 2·4 s [3] (—NCH_3). [Found: C, 81·35; H, 7·1; N, 6·0 $C_{17}H_{17}NO$ requires: C, 81·2; H, 6·8; N, 5·6%.]

Dehydration of **13**. A soln of the above alcohol (0·5 g) in $CHCl_3$ (50 ml) was saturated with HCl. Removal of the solvent and basification of the residue gave **14** as a colourless solid (0·3 g), which crystallized from $CHCl_3$ as small prisms, m.p. 99–101°, λ_{max} (ε) nm, 226 (24,000), 258 (60,000), 302 (16,000), λ_{max} cm^{-1}, 1615 (>C=C<); NMR ($CDCl_3$) ppm, 8·5 multiplet [2] (C_1—H and C_{11}—H); 7·6–7 multiplet [6] (aromatic protons); 3·75 s [4] (2 × (>N—CH_2—); 2·4 s [3] (>N—CH_3). [Found: C, 87·5; H, 6·5; N, 6·0 $C_{17}H_{15}N$ requires: C, 87·5; H, 6·5; N, 6·0], M.W. (mass spec): obs. 233 requires 233.

5-Methyl-4,6-diketodibenz[de,g]*isoquinoline* (**15**, Z = NMe). To a warm 30% aqueous soln of $MeNH_2$ (10 ml) 4,6-diketophenanthro [1,10*c*–*d*] pyran[8] (2 g) was added with stirring. After 30 min the soln was filtered and the solid product recrystallized from MeOH to give **15** (Z = NMe) as colourless cubes (2·1 g) m.p. 221–222° λ_{max} (ε) nm 240 (15,000), 265 (12,000), 340 (9,000), ν_{max} cm^{-1}, 1710, 1670; NMR ($CDCl_3$) ppm, ~8·7 m [4] (C_1—H, C_3—H, C_7—H, C_{11}—H); ~7·7 m [4] (C_2—H, C_8—H, C_9—H, C_{10}—H); 3·5 s [3] (NCH_3). [Found: C, 77·8; H, 4·4; N, 5·1 $C_{17}H_{11}NO_2$ requires: C, 78·1; H, 4·25; N, 5·3%].

5-Methyl-4,6H-dibenz[d,e]*anthracene* (**14**) LAH (1·5 g) was added in small portions to a suspension of the above product (0·3 g) in ether (150 ml). After heating under reflux for 48 hr the soln was cooled and excess reagent destroyed by the addition of 30% sodium potassium tartrate soln. After filtration the etherial soln was evaporated to yield **14** as a colourless solid which recrystallized from $CHCl_3$ as needles (0·17 g) m.p. 99–100°. This compound was identical spectroscopically and chemically with the compound previously obtained from **12** (R = NH_2, R′ = H).

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