Synthetic Routes to Benz- and Naphth-indenoquinolines

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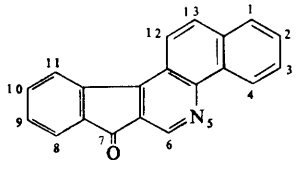
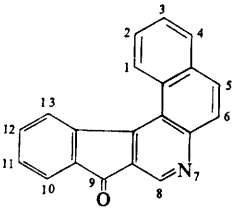
The Mannich base formed *in situ* from indane-1,3-dione, formaldehyde, and piperidine reacted with 1- and 2-naphthylamines in acetic acid to give 7-oxobenz[*h*]- and 9-oxobenz[*f*]-indeno[2,1-*c*]quinolines. Indan-1,3-dione and 2-naphthylamine gave 3-(2-naphthylimino)indan-1-one, converted by treatment with aromatic aldehydes into 13-aryl-12-oxobenz[*f*]indeno[1,2-*b*]quinolines. 1-Naphthylamine and 2-anthrylamine similarly gave 7-aryl-8-oxobenz[*h*]- and 14-aryl-13-oxonaphth[2,3-*f*]-indeno[1,2-*b*]quinolines, respectively. The Mannich bases 2-arylaminomethyl-*N*-(3-oxoinden-1-yl)indane-1,3-dione were isolated from the reaction product of indane-1,3-dione and formaldehyde with aromatic amines.

BENZ- and naphth-indenoquinolines were required for study. However, only some derivatives of 12*H*-benz[*f*]-, 7*H*-benz[6,7]-, and 13*H*-benz[4,5]-indeno-[1,2-*b*]quinolines [1,2] have been synthesised, and the naphthindenoquinolines have not been reported. 2-Methylenecyclohexanone has been successfully utilised [3] in a variant of the Kenner tetrahydrophenanthridine synthesis [4] and it was therefore considered that the similar *in situ* preparation of 2-methyleneindane-1,3-dione followed by reaction with arylamines constituted a suitable approach. It was found that the Mannich base formed *in situ* from indane-1,3-dione, formaldehyde, and piperidine in absolute ethanol reacted with 1- and 2-naphthylamines in glacial acetic acid to give 7-oxobenz[*h*]- (I) and 9-oxobenz[*f*]-indeno[2,1-*c*]quinoline (II), respectively.



(I)



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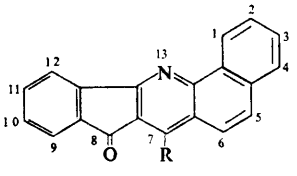

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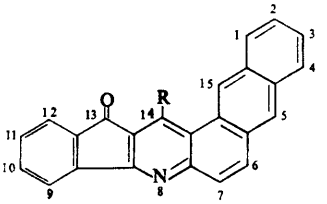
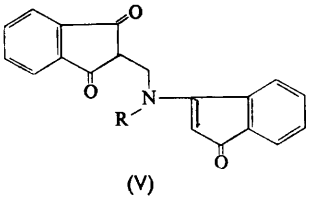
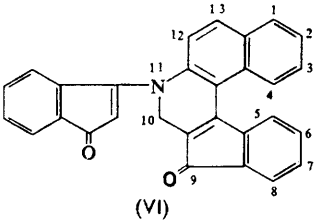


(IV)

An alternative route was sought in the reaction of 3-aryliminoindanones [5] with aromatic aldehydes, since in acridine synthesis [6] ring closure involves diarylamines rather than diarylmethanes. Spectrophotometric evidence favours the anil form [7] for 3-aryliminoindanones; this entails a reactive position *ortho* to the anil, for ring closure. 3-(2-Naphthylimino)indan-1-one, prepared from indan-1,3-dione and 2-naphthylamine, was successfully converted into 13-phenyl-, 13-*o*-nitrophenyl-, and 13-*p*-nitrophenyl-12-oxobenz[*f*]indeno[1,2-*b*]quinoline on treatment with benzaldehyde and its *o*- and *p*-nitro-derivatives. 1-Naphthylamine similarly gave 7-phenyl- and 7-*p*-nitrophenyl-8-oxobenz[*h*]indeno[1,2-*b*]quinolines (III; R = Ph or *p*-$NO_2 \cdot C_6H_4$). The reaction was successfully carried out with 2-anthrylamine, to give 14-*o*-nitro- and 14-*p*-nitro-phenyl-13-oxonaphth[2,3-*f*]indeno-[1,2-*b*]quinolines [IV; R = *o*- or *p*-$NO_2 \cdot C_6H_4$). Wolff-Kishner reduction of (III; R = Ph) gave 7-phenyl-8*H*-benz[*h*]indeno[1,2-*b*]quinoline. The use of formaldehyde in the reaction of indane-1,3-dione with aromatic amines in glacial acetic acid resulted in the isolation of the Mannich bases 2-arylaminomethyl-*N*-(3-oxoinden-1-yl)indane-1,3-dione (V). These compounds do not give colour reactions [8] with amino-acids and primary aromatic amines characteristic of $\Delta^{1',2}$-bi-indane-1,3,3'-trione,[9] and they could not be synthesised from the latter by reaction with formaldehyde and aromatic amines. These findings exclude a $\Delta^{1',2}$-bi-indane-1,3,3'-trione type of structure for these derivatives. Treatment of (V; R = 2-naphthyl) with alcoholic sodium hydroxide or hydrochloric acid in glacial acetic acid led to ring closure, to give 10,11-dihydro-9-oxo-*N*-(3-oxoinden-1-yl)benz-[*f*]indeno[2,1-*c*]quinoline (VI). (VI) is directly obtained, together with (V; R = 2-naphthyl), from the



(V)



(VI)

reaction of indane-1,3-dione (2 mol.) with formaldehyde and 2-naphthylamine (1 mol.) when the reaction time is prolonged. (V; R = 2-naphthyl) is readily prepared

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from 3-(2-naphthylimino)indan-1-one by reaction with formaldehyde and indane-1,3-dione.

EXPERIMENTAL

9-Oxobenz[f]indeno[2,1-c]quinoline.— Indane-1,3-dione (1·46 g., 0·01 mole), piperidine (0·85 g., 0·01 mole), and 30% formaldehyde (1 ml.) in absolute ethanol (50 ml.) were refluxed for 0·5 hr. The ethanol was removed by distillation and a solution of 2-naphthylamine (1·43 g., 0·01 mole) in glacial acetic acid (50 ml.) was added. The solution was refluxed for a further 1 hr., concentrated, and treated with aqueous ethanol. The separated *product* gave yellow needles, m. p. 267° (decomp.) (from acetic acid–ethanol) (Found: C, 85·0; H, 4·0; N, 4·5. $C_{20}H_{11}NO$ requires C, 85·4; H, 3·9; N, 4·9%). The *phenylhydrazone* formed yellow prisms, m. p. 199° (decomp.) (Found: C, 83·8; H, 4·5; N, 11·0. $C_{26}H_{17}N_3$ requires C, 84·0; H, 4·5; N, 11·3%).

7-Oxobenz[h]indeno[2,1-c]quinoline.— This compound was similarly prepared as brownish yellow *prisms*, m. p. >300° (Found: C, 85·4; H, 4·2; N, 4·9%).

3-(2-Naphthylimino)indan-1-one.—Indane-1,3-dione (1·46 g., 0·01 mole) and 2-naphthylamine (1·43 g., 0·01 mole) in glacial acetic acid (50 ml.) were heated to boiling. The solution was concentrated by distillation under reduced pressure from the water-bath. Crystallisation of the residue from acetic acid–ethanol gave the *anil*, as deep blue prisms, m. p. 230° (Found: C, 84·1; H, 4·3; N, 4·8. $C_{19}H_{13}NO$ requires C, 84·1; H, 4·7; N, 5·1%).

13-Phenyl-12-oxobenz[f]indeno[1,2-b]quinoline.— Indane-1,3-dione (1·46 g., 0·01 mole) and 2-naphthylamine (1·43 g., 0·01 mole) in glacial acetic acid (50 ml.) were boiled for a few min. Benzaldehyde (1·1 g., 0·01 mole) was added and the solution was refluxed for 1 hr., concentrated, and treated with aqueous ethanol. The separated *benzindenoquinoline* formed yellow needles, m. p. 295° (decomp.) (from acetic acid) (Found: C, 87·5; H, 4·3; N, 3·8. $C_{26}H_{15}NO$ requires C, 87·3; H, 4·2; N, 3·9%). The 13-o-*nitrophenyl derivative* crystallised in yellow prisms, m. p. >300° (Found: C, 77·3; H, 4·0; N, 6·5. $C_{26}H_{14}N_2O_3$ requires C, 77·6; H, 3·5; N, 6·9%). The 13-p-*nitrophenyl derivative* separated from acetic acid as yellow needles, m. p. >300° (Found: C, 77·5; H, 3·8; N, 6·7%).

7-Phenyl-8-oxobenz[h]indeno[1,2-b]quinoline (III; R = Ph).—This compound was prepared likewise from 1-naphthylamine as yellow *needles*, m. p. 252° (decomp.) (Found: C, 87·0; H, 4·0; N, 3·9%). The p-*nitrophenyl derivative* crystallised as yellow needles, m. p. >300° (Found: C, 77·5; H, 3·7; N, 7·0%).

14-o-Nitrophenyl-13-oxonaphth[2,3-f]indeno[1,2-b]quinoline (IV; R = *o*-NO_2·C_6H_4).—This compound was similarly prepared from 2-anthrylamine as orange-red *plates*, m. p. 299° (decomp.) (from acetic acid) (Found: C, 80·2; H, 3·6; N, 6·1. $C_{30}H_{16}N_2O_3$ requires C, 79·6; H, 3·54; N, 6·1%). The 14-p-*nitrophenyl derivative* formed orange needles, m. p. >300° (Found: C, 80·1; H, 3·5; N, 6·1%).

N-(3-Oxoinden-1-yl)-2-(2-naphthylaminomethyl)indane-1,3-dione.—Indane-1,3-dione (2·9 g., 0·02 mole), 30% formaldehyde (1 ml.), and 2-naphthylamine (1·43 g., 0·01 mole) in glacial acetic acid (200 ml.) were refluxed for 3 hr. Most of the solvent was removed by distillation and the residue was treated with aqueous ethanol. The product separated as red-brown *needles*, m. p. 300° (decomp.) (from acetic acid) (Found: C, 79·7; H, 4·3; N, 3·0. $C_{29}H_{19}NO_3$ requires C, 81·1; H, 4·4; N, 3·2%). The substance is also obtained when a solution of 3-(2-napthylimino)indan-1-one (1·3 g., 0·01 mole), 30% formaldehyde (0·5 ml.), and indane-1,3-dione (0·73 g., 0·01 mole) in glacial acetic acid (80 ml.) is refluxed for 0·5 hr. The p-*chlorophenyl derivative* formed yellow needles, m. p. >300° (Found: C, 72·3; H, 4·1; Cl, 8·9; N, 3·7. $C_{25}H_{16}ClNO_3$ requires C, 72·5; H, 3·8; Cl, 8·5; N, 3·3%). The p-*acetamidophenyl derivative* separated as yellow needles, m. p. 271° (decomp.) (Found: C, 73·9; H, 4·9; N, 6·0. $C_{27}H_{20}N_2O_4$ requires C, 74·3; H, 4·6; N, 6·4%). The o-*methylphenyl derivative* formed yellow prisms, m. p. 283° (decomp.) (Found: C, 79·1; H, 5·2; N, 3·3. $C_{26}H_{19}NO_3$ requires C, 79·3; H, 4·8; N, 3·5%). The p-*methylphenyl derivative* crystallised as yellow needles, m. p. 252° (decomp.) (Found: C, 79·0; H, 5·0; N, 3·3%).

7-Phenyl-8H-benz[h]indeno[1,2-b]quinoline.—The compound (III; R = Ph) (0·6 g.), 50% hydrazine hydrate (5 ml.), and sodium hydroxide (2 g.) in ethylene glycol (80 ml.) were heated under reflux at 190° for 3 hr. The solution, which turned green at the beginning, became almost colourless towards the end of the reaction. It was cooled and diluted with water, and the separated *product* was filtered off and washed, to give yellow platelets, m. p. 178° [from acetic acid–ethanol (intense blue fluorescence)] (Found: C, 90·8; H, 4·9; N, 4·0. $C_{26}H_{17}N$ requires C, 90·95; H, 4·9; N, 4·0%).

10,11-Dihydro-9-oxo-N-(3-oxoinden-1-yl)benz[f]indeno-[2,1-c]quinoline.—The compound (V; R = 2-naphthyl) (0·4 g.) was refluxed with 15% alcoholic sodium hydroxide (100 ml.) or a mixture of concentrated hydrochloric acid (30 ml.) and acetic acid (70 ml.) for 1 hr. The *product*, separated from the concentrated solution when cooled, was filtered and washed to give yellow prisms, m. p. 244° (decomp.) (from acetic acid–ethanol) (Found: C, 84·9; H, 4·1; N, 3·4. $C_{29}H_{17}NO_2$ requires C, 84·65; H, 4·1; N, 3·4%).

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