Cyclisation of Schiff Bases containing Amide or Hydroxamic Acid Groups to 1,2-Dihydroquinazolin-4-ones; Thermal Decomposition Reactions of the 1,2-Dihydroquinazolin-4-ones

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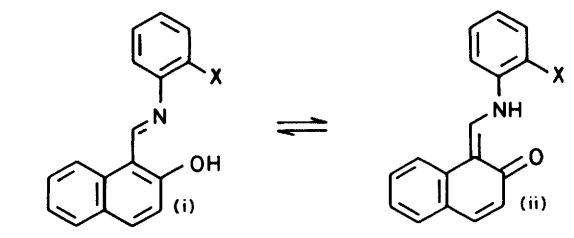
2-Hydroxynaphthalene-1-carbaldehyde reacts with *o*-aminobenzamide in methanol to produce the Schiff base (**1a**) whereas reaction with 2-aminobenzohydroxamic acid leads directly to the dihydrohydroxyquinazolinone (**2b**). The Schiff base (**1b**), an intermediate in the formation of (**2b**), can be isolated (in an impure form) by quenching the reaction with water. When refluxed in dichlorobenzene the dihydrohydroxyquinazolinone (**2b**) decomposes in part by carbon–carbon bond fission to give 3-hydroxyquinazolin-4(3*H*)-one (**5**) and 2-naphthol and to a lesser extent by dehydration leading to the quinazolinone (**4**). The dihydroquinazolinone (**2a**) is readily prepared by cyclisation of the Schiff base (**1a**) and decomposes thermally to give quinazolin-4(3*H*)-one (**9**) and 2-naphthol. A mechanism for the carbon–carbon bond cleavage observed in the thermal decompositions is proposed.

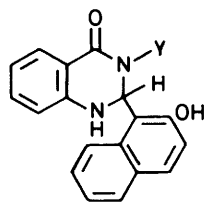
The formation of Schiff bases of the type (**1**) from reaction of 2-hydroxynaphthalene-1-carbaldehyde with aromatic amines has been reported for X = CO_2H, CO_2Me, OH, and SO_3H,[1–5] and the metal complexation properties of the tridentate ligands have been extensively studied.[5–9] In particular, there has been considerable interest in the development of metal complexes of Schiff bases of type (**1**)[10–12] as pigments with extremely high stability to light, heat, and solvents, two of which, C.I. Pigments Yellow 117 and 129, whose structures remain undisclosed, have achieved commercial application in the colouration of automotive finishes and other high grade paints. We were interested in preparing the amide (**1a**) and hydroxamic acid (**1b**) derivatives with a view to investigating their potential as tridentate ligands for the formation of metal complex pigments. In this paper we now describe the preparation of compounds (**1a**) and (**1b**), the cyclisation of the compounds to dihydroquinazolinone derivatives, and thermal decomposition reactions of the dihydroquinazolinones.

Reaction of *o*-aminobenzamide with 2-hydroxynaphthalene-1-carbaldehyde in refluxing methanol resulted in the efficient formation of the yellow compound (**1a**), which exhibits the expected spectroscopic properties. In particular, the presence of two carbonyl resonances at δ 169.24 and 172.18 in the ^{13}C n.m.r. spectrum of (**1a**) suggests that the compound exists predominantly in the enamine tautomeric form (ii).[13,14] Treatment of (**1a**) with a range of first row transition metal acetates under a variety of conditions did not, however, give complexes of definite composition, presumably owing to the poor donor ability of the amide function.

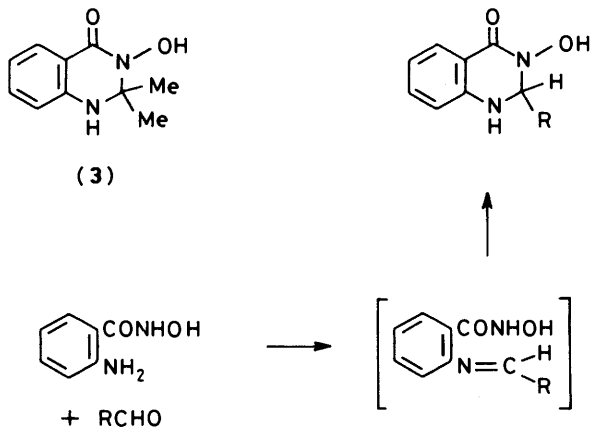
The hydroxamic acid group is known to co-ordinate strongly to metal ions[15] and consequently it was expected that the related Schiff base (**1b**) would form discrete, isolable complexes. In a Dutch patent,[16] the reaction of 2-aminobenzohydroxamic acid with a number of aromatic aldehydes is reported to lead to formation of 1,2-dihydro-3-hydroxyquinazolin-4(3*H*)-ones by cyclisation of the intermediate Schiff bases (Scheme 1). No spectroscopic evidence for the structure of the products was provided and no attempt was made to isolate the Schiff base intermediates. The direct synthesis of another dihydrohydroxyquinazolinone (**3**) from 2-aminobenzohydroxamic acid and acetone has also been reported.[17] We chose to attempt the synthesis of the hydroxamic acid Schiff base derivative (**1b**) with a view to subsequent preparation of its metal complexes.



(**1**) a ; X = $CONH_2$
b ; X = CONHOH



(**2**) a ; Y = H
b ; Y = OH



(**3**)

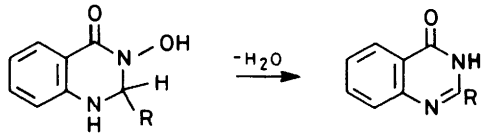
Scheme 1.

Under a range of conditions, the reaction of 2-aminobenzohydroxamic acid with 2-hydroxynaphthalene-1-carbaldehyde was found to lead directly to the cyclised product, 1,2-dihydro-3-hydroxy-2-(2-hydroxy-1-naphthyl)-quinazolin-4(3*H*)-one (**2b**), characterised by i.r., ^1H and ^{13}C n.m.r., and mass spectroscopy. The ^{13}C n.m.r. spectrum of (**2b**) exhibits a peak at δ 68.68, characteristic of an sp^3 carbon, attributed to C-2, and the singlet at δ 6.35 in the ^1H n.m.r. spectrum corresponds to 2-H. In an attempt to detect the proposed intermediate Schiff base (**1b**), which was expected to exhibit a double absorption in the range 430—470 nm similar to that observed ($\lambda_{max.}$ 445 and 455 nm) in the spectrum of the related compound (**1a**), the reaction was carried out in a u.v./visible spectrophotometer; however, no such absorptions were detected during the course of the reaction, carried out under a range of conditions. It is proposed therefore, that the Schiff base (**1b**) is formed but, since it rapidly undergoes cyclisation to the dihydroquinazolinone (**2b**), no significant concentration of the intermediate is observed. However, when 2-aminobenzohydroxamic acid and 2-hydroxynaphthalene-1-carbaldehyde were refluxed in methanol for 30 min and the reaction was then quenched by addition of an equal volume of water, a yellow solid was obtained which it is proposed, on the basis of its spectroscopic properties, contains the Schiff base (**1b**) as the major component.

In particular, the absorption at 1 663 cm^{-1} in the i.r. spectrum is consistent with the hydroxamic acid carbonyl group, and the peak at 1 621 cm^{-1} is assigned to the naphthalene ring carbonyl stretching vibration of the enamine tautomer (ii), while the diffuse reflectance visible spectrum of the yellow solid is very similar to that of the Schiff base amide derivative (**1a**). The Schiff base (**1b**) appeared to be quite stable in the solid state but was highly unstable in solution, preventing purification by recrystallisation or chromatographic methods. That this instability is due to rapid cyclisation to the dihydroquinazolinone (**2b**) is demonstrated by the solution spectroscopic evidence. The u.v./visible spectrum recorded immediately after solution in ethanol at room temperature exhibited strong absorptions at 442 and 461 nm similar to those shown in the spectrum of (**1a**), which extremely rapidly diminished in intensity. The spectrum after 30 min consisted only of absorptions characteristic of the cyclised product (**2b**). The ^1H n.m.r. spectrum of the material recorded 5 min after dissolution in $(CD_3)_2SO$ was identical with that of the dihydrohydroxyquinazolinone (**2b**). It is proposed that the cyclisation of Schiff base (**1b**) to the dihydrohydroxyquinazolinone (**2b**) is a solvent-dependent equilibrium. In refluxing methanol, the cyclisation reaction is strongly favoured, formation of (**2b**) being further assisted by crystallisation of the product from solution. In contrast, the reverse reaction, ring opening of (**2b**), is promoted by addition of water and subsequent precipitation of the resulting Schiff base (**1b**).

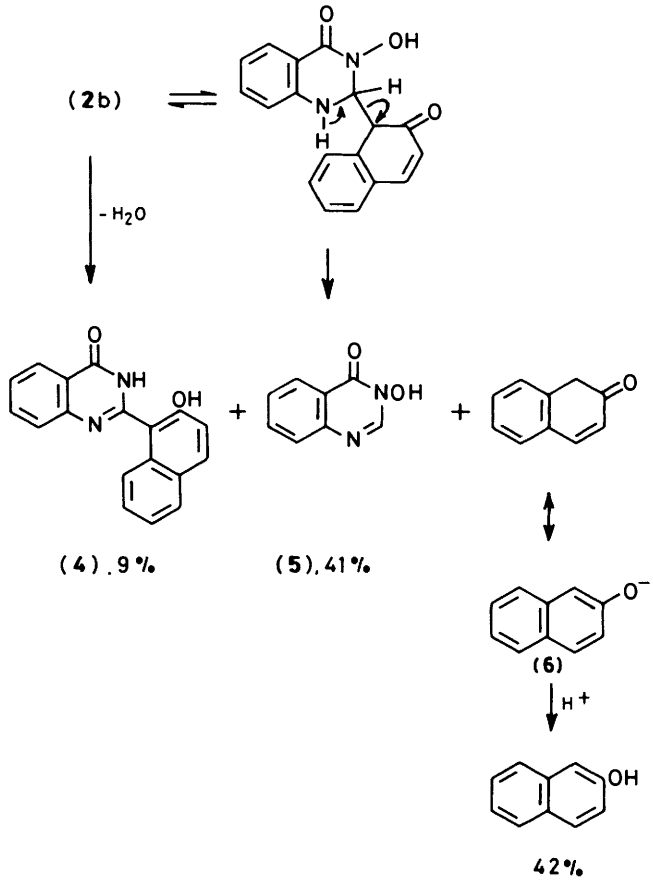
Attempts to prepare copper(II) complexes of compound (**1b**) using template procedures, in the hope that rapid reaction *in situ* of the Schiff base formed with the metal ion and precipitation of the resulting complex might prevent cyclisation to compound (**2b**), were unsuccessful. The copper-containing products of these reactions were indeterminate in composition although similar in i.r. spectroscopic properties to those prepared directly from reaction of copper(II) salts with compound (**2b**), suggesting that the cyclisation had indeed taken place. However, no characterisable complexes of compound (**2b**) could be prepared, reflecting the complicated arrangement of donor atoms in the molecule offering numerous possibilities for metal–ligand interactions.

Differential scanning calorimetric investigation of the dihydrohydroxyquinazolinone (**2b**) showed that the compound underwent a strongly exothermic decomposition immediately following the melting endotherm at 163 °C. It was of interest to investigate the course of this thermal decomposition, particularly as the previously mentioned patent[16] claims that 2-substituted 1,2-dihydro-3-hydroxyquinazolin-4(3*H*)-ones undergo dehydration on azeotropic distillation leading to quinazolin-4-ones although no supporting experimental description or product characterisation was provided (Scheme 2). We now report that the dihydrohydroxyquinazolinone (**2b**),



Scheme 2.

treated at reflux in 1,2-dichlorobenzene for 6 h using a Dean-Stark apparatus, gave the expected dehydration product 2-(2-hydroxy-1-naphthyl)quinazolin-4(3*H*)-one (**4**) although only in 9% yield. The major products of the reaction (Scheme 3) were

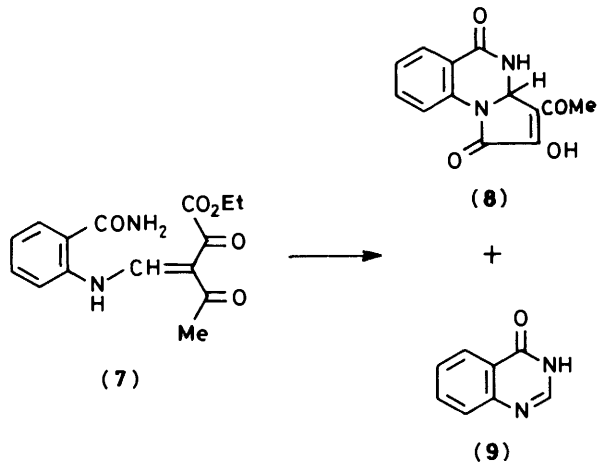


Scheme 3.

3-hydroxyquinazolin-4-(3*H*)-one (**5**) and 2-naphthol, both being isolated in *ca.* 40% yield. A proposed mechanism for the formation of these major products is given in Scheme 3. It is suggested that carbon–carbon bond cleavage occurs in the keto tautomer of the dihydrohydroxyquinazolinone (**2b**), the bond fission being facilitated by the formation of the resonance-stabilised carbanion (**6**), which is subsequently protonated to give 2-naphthol. It is interesting that the mass spectrum of compound (**2b**), in addition to the peak for the molecular ion

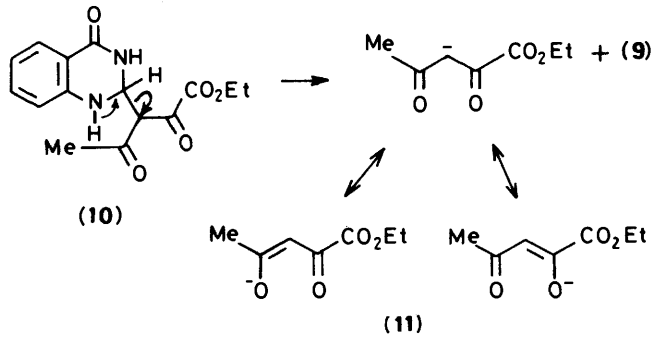
(*m/z* 306), shows prominent peaks at *m/z* 288 corresponding to loss of water, and peaks at *m/z* 162 and 144. It is likely that these last two peaks are due to the molecular ions of 3-hydroxyquinazolin-4(3*H*)-one (**5**) and 2-naphthol respectively, formed by thermal decomposition of (**2b**) on the mass spectrometer probe.

Kurihara *et al.*[18] have recently reported the double cyclisation of ethyl 3-(2-carbamoylanilino)methylene-2,4-dioxovalerate (**7**) to produce 3-ethanoyl-3a,4-dihydro-2-hydroxypyrrolo[1,2-*a*]quinazoline-1,5(2*H*,2a*H*)-dione (**8**) in 12—84% yield depending on reaction conditions (Scheme 4). In



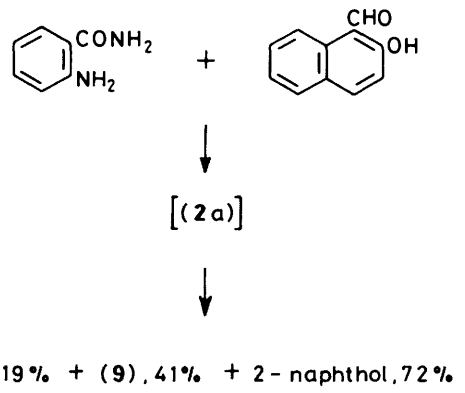
Scheme 4.

addition, the authors report the formation of quinazolin-4(3*H*)-one (**9**) in up to 70% yield as a side product, but they do not discuss the origin of this compound. It would appear that a carbon–carbon bond cleavage similar to that described in Scheme 3 also operates in this case. The formation of (**8**) from (**7**) proceeds *via* an initial cyclisation to give the dihydroquinazolinone (**10**). Carbon–carbon bond cleavage is then facilitated by the formation of the resonance-stabilised carbanion derived from ethyl 2,4-dioxopentanoate (**11**) (Scheme 5).



Scheme 5.

The structure of the 2-substituted quinazolinone (**4**) was confirmed by independent synthesis using the general method for quinazolinones described by Imai[19] in which an aldehyde is treated with 2-aminobenzamide in dimethylacetamide at 150 °C in the presence of sodium hydrogen sulphite. Reaction of 2-aminobenzamide with 2-hydroxynaphthalene-1-carbaldehyde under these conditions led to compound (**4**) in 19% yield although the major products of this reaction were 2-naphthol (72%) and quinazolin-4(3*H*)-one (**9**) (41%) (Scheme 6).



Scheme 6.

The formation of quinazolinones by this route is suggested to proceed *via* an intermediate dihydroquinazolinone which undergoes dehydrogenation to provide the quinazolinone.[19] It would appear that reaction of 2-aminobenzamide with 2-hydroxynaphthalene-1-carbaldehyde using Imai's conditions leads to formation of the intermediate (**2a**) which can undergo either dehydrogenation to (**4**), or carbon–carbon bond cleavage by a mechanism similar to that previously described, to give the unsubstituted quinazolinone (**9**) and 2-naphthol. In order to confirm this suggestion we have prepared the dihydroquinazolinone (**2a**) by an independent route and investigated its thermal decomposition.

Under relatively mild conditions the Schiff base (**1a**) cyclises to afford the dihydroquinazolinone (**2a**) in good yield. The ^{13}C n.m.r. spectrum of (**2a**) exhibits a resonance at δ 60.83 corresponding to C-2 which is adjacent to N–H and, therefore, is less deshielded than the corresponding carbon in compound (**2b**) (δ 69.68) which is adjacent to N–OH. Similarly the singlet at δ 6.73 in the ^1H n.m.r. spectrum of (**2a**), is attributed to 2-H which experiences less deshielding than the corresponding proton in the 3-hydroxy derivative (**2b**), (δ 6.98) Differential scanning calorimetric examination of dihydroquinazolinone (**2a**) shows that it undergoes exothermic decomposition immediately following the melting endotherm at *ca.* 195 °C. Refluxing (**2a**) in dichlorobenzene for 6 h under nitrogen led, as expected, to 2-naphthol and quinazolin-4(3*H*)-one (**9**) as a result of a thermal carbon–carbon bond fission. It is interesting that the mass spectrum of the dihydroquinazolinone (**2a**) which exhibits a peak at *m/z* 290 corresponding to the molecular ion also shows strong peaks at *m/z* 146 and 144. These are likely to correspond to the molecular ions of quinazolin-4(3*H*)-one (**9**) and 2-naphthol respectively formed by thermal decomposition of (**2a**) on the mass spectrometer probe. Further investigation into the scope of these thermal decomposition reactions is in progress.

Experimental

M.p.s are extrapolated onset temperatures determined using a Mettler DSC 30 differential scanning calorimeter. I.r. spectra were recorded as KBr discs with a Perkin-Elmer 599B spectrophotometer. ^1H N.m.r. spectra were recorded on a Perkin-Elmer R32 spectrometer for solutions in $(CD_3)_2SO$ using tetramethylsilane as internal reference. ^{13}C N.m.r. spectra were obtained for $(CD_3)_2SO$ solutions on a Brooker WP200SY instrument. Mass spectra were measured using an AEI MS902

spectrometer. U.v. spectra were recorded in ethanol solution on a Pye Unicam SP 800A spectrophotometer. Reflectance spectra for powder samples were obtained using a Pye Unicam SP 8-200 spectrophotometer with Kodak $BaSO_4$ standard white paint as reference. C, H, and N analyses were performed by the Department of Applied Chemical Sciences, Napier College, Edinburgh.

o-(2-*Hydroxy*-1-*naphthylmethyleneamino*)*benzamide* (**1a**).—*o*-Aminobenzamide (1.98 g, 14.5 mmol) and 2-hydroxynaphthalene-1-carbaldehyde (2.50 g, 14.5 mmol) in methanol (75 cm^3) were refluxed for 1 h. The yellow precipitate was filtered off, washed with methanol, and dried *in vacuo* to give the *title compound* (**1a**) (3.27 g, 78%), as yellow needles from ethanol, m.p. 202 °C (decomp.) (Found: C, 74.3; H, 4.7; N, 9.7. $C_{18}H_{14}N_2O_2$ requires C, 74.4; H, 4.8; N, 9.6%); $\nu_{max.}$ 3 380, 3 165 (NH_2), 1 660 (amide C=O), and 1 618 cm^{-1} (C=O); $\lambda_{max.}$ 229, 255 (sh), 317, 335 (sh), 357, 440, and 455 nm; δ_H 3.30 (2 H, s, NH_2), 6.84 (1 H, d, phenyl 6-H), 7.15—7.86 (8 H, m, ArH), 8.34 (1 H, d, naphthyl 8-H), 9.36 (1 H, s, =CH–N), and 14.90 (1 H, br s, NH); δ_C 108.89, 119.10, 120.26, 123.09, 123.50, 125.58, 126.66, 128.20, 128.41, 129.08, 131.26, 133.60, 137.41, 142.10 (aromatic C), 153.79 (=CH–N), 169.24 (ring C=O), and 172.18 ($CONH_2$). Note that the spectral data have been interpreted in terms of the ketoenamine structure (**1a**) (ii).

1,2-*Dihydro*-3-*hydroxy*-2-(2-*hydroxy*-1-*naphthyl*)*quinazolin*-4(3H)-*one* (**2b**).—2-Aminobenzohydroxamic acid[20] (2.50 g, 16.5 mmol) and 2-hydroxynaphthalene-1-carbaldehyde (2.85 g, 16.5 mmol in methanol (100 cm^3) were refluxed for 1 h. The pale yellow precipitate which separated on cooling was filtered off and washed with cold methanol (10 cm^3). Recrystallisation from methanol afforded the *title compound* (**2b**), (4.80 g, 95%) as white crystals, m.p. 163 °C (Found: C, 70.3; N, 4.6; N, 9.0. $C_{18}H_{14}N_2O_3$ requires C, 70.6; H, 4.6; N, 9.2%); $\nu_{max.}$ 3 440 (OH), 3 220 (NH), and 1 645 cm^{-2} (C=O); $\lambda_{max.}$ 225, 253 (sh), and 316 nm; δ_H 6.68 (1 H, d, 8-H), 9.50 (1 H, br s, OH), and 10.81 (1 H, s, OH); δ_C 68.68 (2-C), 113.51, 113.74, 114.14, 117.28, 118.19, 122.63, 125.21, 125.77, 127.68, 128.36, 128.78, 130.77, 133.19, 133.48, 148.13, 154.86 (aromatic C), and 165.23 (C=O); *m*/*z* 306 (M^+), 298, 245, 162, and 144.

Isolation of the Schiff Base Intermediate (**1b**).—A mixture of 2-aminobenzohydroxamic acid (2.50 g, 16.5 mmol)[20] and 2-hydroxynaphthalene-1-carbaldehyde (2.85 g, 16.5 mmol) in methanol (50 cm^3) was refluxed for 30 min and then diluted with water (50 cm^3). The yellow precipitate was filtered off and dried *in vacuo* to give a product (2.83 g); $\nu_{max.}$ 3 250 (NHOH), 3 050 (NHOH), 1 663 (C=O), and 1 621 cm^{-1} (C=N or ring C=O if in ketoenamine tautomer); $\lambda_{max.}$ (solution) 442 and 461 nm. These visible absorptions diminish rapidly in intensity and have virtually disappeared after 5 min, the spectrum after 30 min being identical with that of the dihydroquinazolinone (**2b**). The ^1H n.m.r. spectrum of a sample recorded 5 min after dissolution exhibited only signals corresponding to the dihydroquinazolinone (**2b**). Purification of the product by recrystallisation or chromatographic techniques proved impossible owing to its instability in common solvents. On the basis of the above spectroscopic evidence it is proposed that the isolated product is largely the Schiff base intermediate (**1b**) which undergoes rapid cyclisation in solution to give the dihydroquinazolinone (**2b**).

2-(2-*Hydroxy*-1-*naphthyl*)*quinazolin*-4(3H)-*one* (**4**).—2-Hydroxynaphthalene-1-carbaldehyde (5.16 g, 30 mmol), *o*-aminobenzamide (4.08 g, 30 mmol), and sodium hydrogen sulphite (4.68 g, 45 mmol) were heated in dimethylacetamide (45 cm^3) at 150 °C for 2 h. The mixture was cooled and poured into toluene (100 cm^3) and 10% aqueous sodium chloride (100 cm^3). Filtration of the two phase mixture afforded the *title compound* (**4**) (1.62 g, 19%) as white prisms from 2-methoxyethanol, m.p. 309 °C (Found: C, 75.2; H, 4.3; N, 9.9. $C_{18}H_{12}N_2O_2$ requires C, 75.0; H, 4.2; N, 9.7%); $\nu_{max.}$ 3 475 (NH), 3 050br (OH), and 1 672 cm^{-1} (C=O); δ_H 3.44 (1 H, br s, NH), 7.24—7.98 (9 H, m, ArH), 8.25 (1 H, d, 3-naphthyl 8-H), and 11.40 (1 H, br s, OH); δ_C 114.76, 118.33, 121.45, 123.06, 123.43, 125.85, 126.61, 127.12, 127.27, 127.46, 128.03, 131.09, 132.43, 134.41, 149.13, 152.11, 153.36 (aromatic ring C), and 162.09 (C=O); *m*/*z* 288 (M^+), 287, 259, 161, 144, 120, and 115. The organic and aqueous layers of the filtrate were separated and the organic layer was dried (Na_2SO_4) and evaporated. The residue was chromatographed on a column of alumina (25 × 1.8 cm) using ether as eluant to give colourless eluates which afforded 2-naphthol (3.10 g, 72%), m.p. 122 °C (lit.,[21] 123 °C). The aqueous extract was evaporated to *ca.* 50 cm^3. The resulting suspension was filtered at 60 °C to remove inorganic salts, and the filtrate chilled to give white crystals of quinazolin-4(3*H*)-one (**9**) (1.81 g, 41%), m.p. 215 °C (lit.,[22] 215—216 °C), identical (^1H n.m.r.) with an authentic sample.

1,2-*Dihydro*-2-(2-*hydroxy*-1-*naphthyl*)*quinazolin*-4(3H)-*one* (**2a**).—The benzamide (**1a**) (1.45 g, 1 mmol) was refluxed in ethanol (30 cm^3) under nitrogen for 6 h. The hot reaction mixture was filtered and the white precipitate washed with ethanol and dried *in vacuo* to give the *title compound* (**2a**) (1.20 g, 83%) as white prisms, m.p. 193 °C (exothermic decomp.) (Found: C, 74.7; H, 4.9; N, 9.9. $C_{18}H_{14}N_2O_2$ requires C, 74.5; H, 4.9; N, 9.7%); $\nu_{max.}$ 3 380 (NH), 3 355 (NH), and 1 655 (CO) cm^{-1}; δ_H 3.34 (2 H, br s, NH), 6.73 (3 H, s and d, 2- and 6-H), 7.15—7.92 (6 H, m, ArH), 8.75 (1 H, d, naphthyl 3-H), and 13.00 (1 H, br s, OH); δ_C 60.83 (quinazolinone 2-C), 114.11, 114.56, 115.49, 117.26, 118.08, 122.56, 125.46, 125.85, 127.78, 128.38, 128.92, 130.86, 133.11, 149.78, 154.08 (aromatic ring C), and 164.95 (C=O); *m*/*z* 290 (M^+), 245, 217, 146, 144, 120, and 115.

Thermal Decomposition of 1,2-*Dihydro*-3-*hydroxy*-2-(2-*hydroxy*-1-*naphthyl*)*quinazolin*-4(3H)-*one* (**2b**).—1,2-Dihydro-3-hydroxy-2-(2-hydroxy-1-naphthyl)quinazolin-4(3*H*)-one (**2b**) (0.918 g, 3 mmol) was refluxed under nitrogen in 1,2-dichlorobenzene (60 cm^3) using a Dean-Stark receiver for 6 h. The solution was concentrated to 20 cm^3 and chilled. Filtration gave 3-*hydroxyquinazolin*-4(3*H*)-*one* (**5**) (0.20 g, 41%) as white prisms (from toluene), m.p. 238 °C (lit.,[23] 240 °C) (Found: C, 59.0; H, 3.7; N, 17.4. $C_8H_6N_2O_2$ requires C, 59.2; H, 3.7; N, 17.4%); δ_H 7.45—7.90 (3 H, m, 5-, 6-, and 7-H), 8.18 (1 H, d, 8-H), 8.51 (1 H, s, 2-H), and 11.75 (1 H, br s, OH). The filtrate was applied to a column of alumina (15 × 2.0 cm) and eluted with chloroform–ethanol (19:1) to give colourless eluates which were evaporated to afford 2-naphthol (0.183 g, 42%), m.p. 122 °C (lit.,[21] 123 °C), identical (^1H n.m.r.) with an authentic sample. Further elution with the same solvent gave a colourless fraction, evaporated to give 2-(2-*hydroxy*-1-*naphthyl*)*quinazolin*-4(3H)-*one* (**4**) (0.080 g, 9%), m.p. 309 °C; identical (i.r. spectrum) with sample prepared from reaction of *o*-aminobenzamide and 2-hydroxynaphthalene-1-carbaldehyde in the presence of sodium hydrogen sulphite.

Thermal Decomposition of 1,2-*Dihydro*-2-(2-*hydroxy*-1-*naphthyl*)*quinazolin*-4(3H)-*one* (**2a**).—1,2-Dihydro-2-(2-hydroxy-1-naphthyl)quinazolin-4(3*H*)-one (**2a**) (0.290 g, 1 mmol) was refluxed in 1,2-dichlorobenzene (20 cm^3) under nitrogen for 6 h. The solution was then concentrated to 5 cm^3 and chilled. The precipitate was filtered off and recrystallised from water to give quinazolin-4(3*H*)-one (**9**) (0.082 g, 56%) as white crystals, m.p. 215 °C (lit.,[22] 215—216 °C). The filtrate was applied to a column of alumina (15 × 2.0 cm) and eluted with chloroform–ethanol (19:1) to give colourless eluates which

were evaporated to give 2-naphthol (0.100 g, 69%), m.p. 122 °C (lit.,[21] 123 °C), identical (^{1}H n.m.r.) with an authentic sample.

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