BASE CATALYZED CONDENSATION OF MALONONITRILE AND 2-HYDROXY-1-NAPHTHALDEHYDE WITH DIFFERENT KETONES

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Abstract - Several derivatives of *2H*-phenyl[*f*]chromene-2-carbonitrile, 2*H*-benzo[*f*]chromano[2,3,4:*d*,*e*]pyrido[2,3-*d*]pyrimidine, and benzo[*g*]-2-quinolone were prepared by the direct condensation of malononitrile with 2-hydroxy-1-naphthaldehyde in the presence of various ketones and ammonium acetate. The effect of solvent, ratio of reactant, and different basic catalysts were studied.

Previous papers have shown that pyran derivatives possess pronounced biological properties.[1] On the other hand, substituted pyridines show acaricidal, insecticidal and herbicidal activities.[2] Moreover, pyrimidines are important analgesic and anti-inflammatory agents.[3,4] Compounds having a combination of naphthopyran with pyridine and/or pyrimidine moieties can be expected to possess medicinal properties. In addition, we reported that while malononitrile condenses in a 1:1 molar ratio with cresotaldehyde and methyl ethyl ketone in the presence of ammonium acetate to give substituted benzo[*f*]pyrano-3-carbonitrile derivatives,[5] it reacts with a mixture of cresotaldehyde and methyl ethyl ketone, in the presence of ammonium acetate, to give the substituted nicotinonitrile derivatives.

Thus, as an extension to our previous work,[6] the present manuscript describes the synthesis of some chromenopyridopyrimidine heterocycles via condensation of malononitrile and 2-hydroxy-1-naphthaldehyde with different ketones in the presence of ammonium acetate with a view of establishing their chemical and biological activities. Thus, condensation of 2-hydroxy-1-naphthaldehyde (**1**) with malononitrile in equimolar ratio and in presence of slight excess of ammonium acetate afforded 3-imino-*2H*-[*f*]chromene-2-carbonitrile (**2**) in good yield. When **1**

was heated with an excess of malononitrile, 2-amino-1-cyano-5-cyanomethyl-2*H*-benzo[*f*]-chromano[2,3,4:*d,e*]pyrido[2,3-*d*]pyrimidine (**3**) was obtained as the only main product. On the other hand, when the reaction was carried out in the presence of a catalytic amount of triethylamine (TEA) or piperidine instead of ammonium acetate, compound (**2**) was obtained as the main product. The infrared spectrum of **2** revealed the presence of C=N, C=N, and NH absorptions at 2120, 1650, and 3150 cm^{-1}, respectively, while the ir spectrum of **3** showed bands at 3450, 2220, and 1650 cm^{-1} characteristic for amino, cyano, and imino stretching vibrations, respectively. The ^1H nmr spectrum of **1** as well as those of the other compounds reported in this study were consistent with proposed structures. In those cases where ^{13}C nmr spectrum could be obtained, the resulting spectra were also consistent with proposed structure. In several cases ^{13}C nmr spectra could not be obtained due to the poor solubility of the compounds in common nmr solvents. Refluxing equimolar quantities of a mixture of **1**, malononitrile and acetophenone for 2 h in the presence of a slight excess of ammonium acetate yielded a mixture of 9-12% of compound (**3**), 17-20% of 5-cyanomethyl-2-phenyl-2*H*-benzo[*f*]chromano-[2,3,4:*d,e*]pyrido[2,3-*d*]pyrimidine (**4**) and 12% of 4-imino-2-cyanomethyl-2*H*-benzo[*f*]chromeno-[2,3-*d*]pyrimidine (**5**), respectively. Minimizing reflux time to only 10-15 min afforded a mixture containing 15%, 10%, and 7% of compounds (**2**, **4**, and **5**), respectively; compound **3** could not be detected. All attempts to limit this reaction to the1:1 adduct such as using limited quantities of malononitrile under conditions favorable for monocyclo addition were unsuccessful.

Of the several possibleisomeric structures, structures (**3**, **4**, and **5**) were established for the reaction products based on their spectral data. On the other hand, when this reaction was refluxed for short or long periods in the presence of TEA, **2** was formed as the only main product. The ir spectrum of **4** showed absorption bands in the 1630-1500 and 2220 cm^{-1} regions assignable to stretching vibration of the hetero ring and nitrile moieties, respectively; meanwhile this spectrum did not show absorptions in the amino or imino regions. For compound (**5**), their spectrum showed the characteristic bands for cyano, C=N, and NH groups at 2220, 1650, and 1500 cm^{-1}, respectively. These facts are taken to indicate that in many cases in the present study the course of the reaction was markedly influenced by choice of base catalyst and or reaction time. It seems reasonable to assume that the formation of **2-5** may be achieved by a process where malononitrile first condenses with 2-hydroxy-1-naphthaldehyde to give **2**, which in turn is converted to 3-(2'-amidino)-2-iminobenzo[*f*]chromene (**6**). The latter intermediate condenses with the available ketone, and then reacts with an additional molecule of malononitrile to afford the end product (**4**).

As shown in Scheme 1, the formation of **5** could be interpreted on the bases of the addition of one molecule of malononitrile to the intermediate (**6**). Treatment of compound (**5**) with an additional molecule of malononitrile gave compound (**3**). Moreover, the later product (**3**) could be formed *via* the reaction of the intermediate (**6**) with two molecules of malononitrile. Indeed when heated with acetophenone and ammonium acetate in ethanol, compound (**2**) gave **4**, while the use of cyclopentanone as the ketone reactant, afforded a mixture of **7** (30%) and **5** (15%), respectively. The reaction of **2** with cyclohexanone under similar conditions afforded compound (**8**) as the only main product in 35% yield.

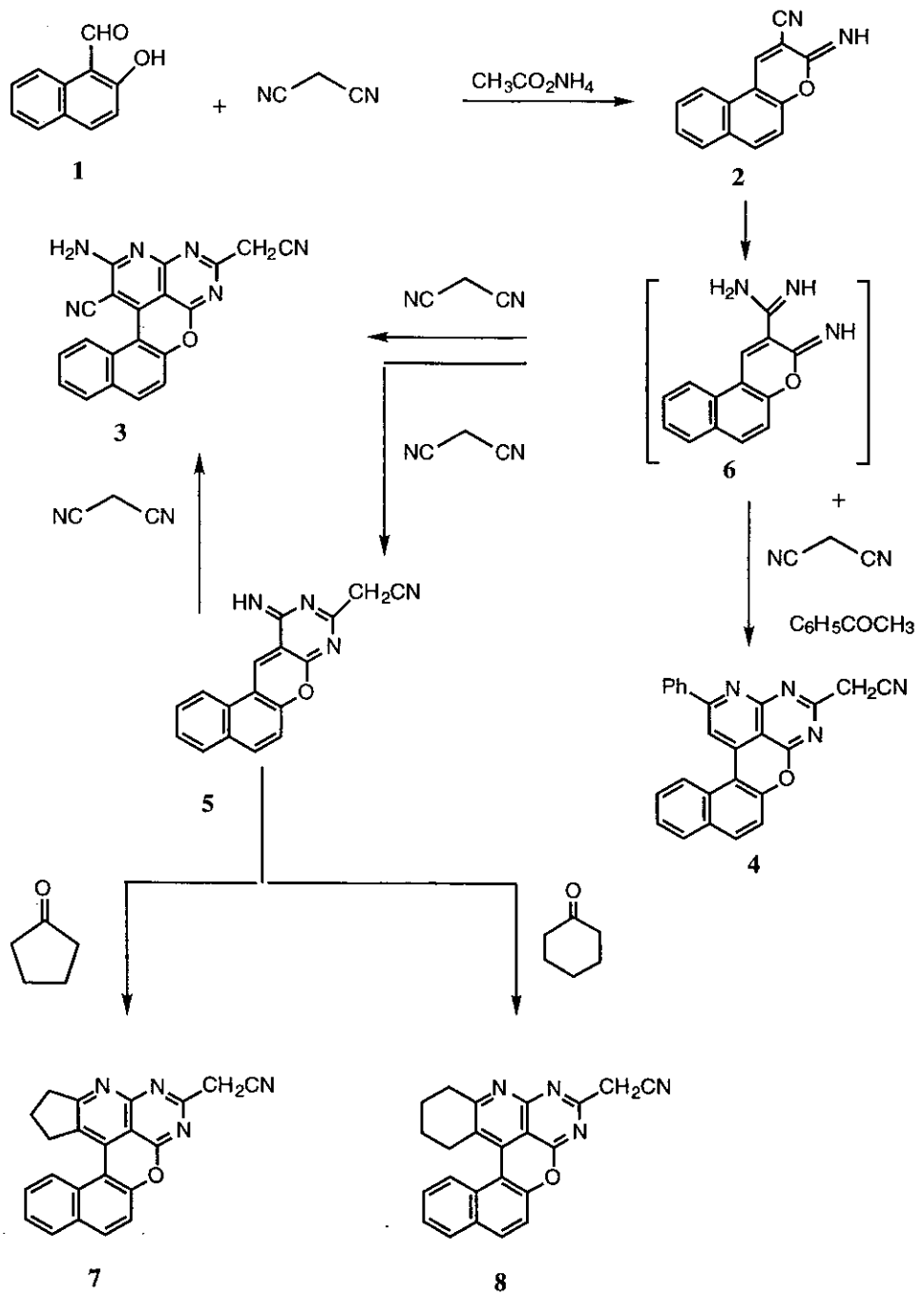
The formation of **7** and **8** was assumed to proceed *via* addition of the α-carbon atom of the ketone molecule to the activated double bond in compound (**5**) followed by cyclocondensation of the produced Michael adduct to the final isolable products (**7**) or (**8**) with the elimination of water. The ir spectra of **7** and **8** showed no absorption bands for amino or imino groups and were very similar to those of compound (**4**).

The behavior of cyanoacetamide and ethyl cyanoacetate upon such condensation was also investigated. The reactions are outlined in Scheme 2. It was found that **1** reacts with cyanoacetamide instead of malononitrile in the presence of ammonium acetate in absolute ethanol to yield 65% of the benzoquinolone derivative (**9**) as a single product (determined by tlc). The ir spectrum of **9** showed absorption bands at 1680, 2220, and 3350 cm^{-1} attributable to the amidic carbonyl, cyano and NH groups, respectively.

Unexpectedly, when compound (**1**) was allowed to react with a mixture of cyanoacetamide and cyclopentanone in absolute ethanol and in presence of ammonium acetate, it gave the 3-carboxamidechromene derivative (**10**) instead of the corresponding cyclopenteno-naphthopyranoquinolone derivative (**11**) in good yield. Using TEA instead of ammonium acetate as a catalyst in the above mentioned reaction afforded two isolable products, (**11**) and its isomeric product (**12**). The formation of these products is assumed to proceed *via* addition of the cyclopentanone C-2 carbon to the activated double bond in **9** and **10** (which is assumed to be formed first) followed by cyclization of the produced Michael adduct to give the required products (**11**) and (**12**), respectively. The structures of **11** and **12** were established not only on the basis of their analytical and spectral data but also on their independent synthesis *via* reaction of either **9** or **10** with cyclopentanone and ammonium acetate in absolute ethanol to give the corresponding **11** and/or **12**, respectively. The ir spectra of **11** and **12** revealed absorption bands nearby 1630-1500, 1680 and 3150 cm^{-1} characteristic of stretching vibrations of the hetero ring, amidic carbonyl and NH function, respectively.

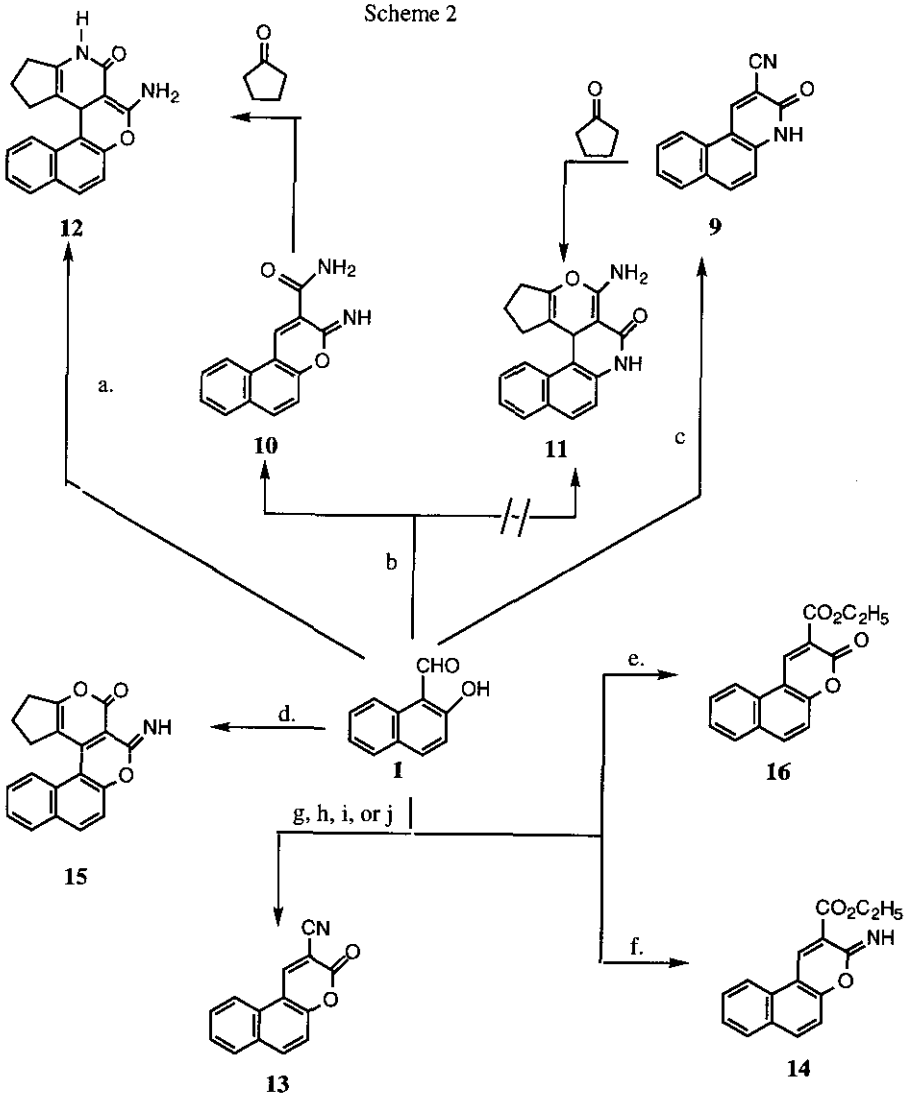
Interestingly, when compound (**1**), cyanoacetamide and ammonium acetate were allowed to

Scheme 1



react with acetophenone, cyclopentanone and/or isopropyl methyl ketone in acetic acid the 3-cyanochromenone derivative (**13**) was obtained as the only isolable product. Its ir spectrum showed two characteristic absorption bands at 1700 and 2220 cm^{-1}, characteristic of carbonyl and cyano groups, respectively. The formation of **13** in such cases indicates that the use of acetic acid as a solvent did not favor any further cycloaddition reaction, and consequently the

Scheme 2



a. $NCCH_2CONH_2$ / cyclopentanone / TEA / C_2H_5OH. b. cyclopentanone / $NCCH_2CONH_2$ / $CH_3CO_2NH_4$ / C_2H_5OH. c. $NCCH_2CONH_2$ / $CH_3CO_2NH_4$ / C_2H_5OH. d. $NCCH_2CO_2C_2H_5$ / cyclopentanone / $CH_3CO_2NH_4$ / C_2H_5OH. e. $NCCH_2CO_2C_2H_5$ / $CH_3CO_2NH_4$ / CH_3CO_2H. f. $NCCH_2CO_2C_2H_5$ / $CH_3CO_2NH_4$ / C_2H_5OH. g. $NCCH_2CONH_2$ / $CH_3CO_2NH_4$ / CH_3CO_2H. h. $NCCH_2CONH_2$ / $C_6H_5COCH_3$ / CH_3CO_2H. i. i-$C_3H_7COCH_3$ / CH_3CO_2H. j. $NCCH_2CO_2C_2H_5$ / cyclopentanone / TEA / CH_3CO_2H.

reaction was stopped at this stage of reaction. On the other hand, when an ethanolic solution of **1** was allowed to react with ethyl cyanoacetate in presence of ammonium acetate, it afforded the 3-carbethoxyquinolone derivative (**14**).

In contrast to the behavior of cyclopentanone with cyanoacetamide, **1** reacted with ethyl cyanoacetate in the presence of ammonium acetate and ethanol to yield the cycloaddition product (**15**). However, when this reaction was repeated in the presence of TEA as a base, **13** was obtain as the only product. Compound (**13**) was synthesized independently *via* hydrolysis

of **2** in a mixture of conc. hydrochloric acid and ethanol. In addition, the reaction of **1** , ethyl cyanoacetate and ammonium acetate in acetic acid afforded the benzocoumarine derivative (**16**). The ir spectrum for this product revealed two absorption bands at 1700 and 1730 cm^{-1} characteristic of cyclic and acyclic carbonyl moieties, respectively.

The procedures described in this investigation were found to be satisfactory for synthesis of a wide variety of polyheterocyclic compounds in good yield.

EXPERIMENTAL

All chemicals were purchased from Aldrich Chemical Company and were distilled or recrystallized prior to use. Melting points were taken on an electrochemical apparatus and are uncorrected. The ir spectra (KBr) were measured on a SP2000 Pye-Unicam spectrophotometer, the nmr spectra were determined on a Brucker WPSY-200 MHz spectrometer using TMS as internal standard, and the elemental analyses were performed at the University of Mansoura University Analytical Services.

Reaction of 2-Hydroxy-1-naphthaldehyde (1) with Malononitrile. A. Preparation of 3-Imino-*2H*-phenyl[*f*]chromene-2-carbonitrile (**2**). A mixture of malononitrile (1.98 g, 0.03 mol), 2-hydroxy-1-naphthaldehyde (**1**, 5.16 g, 0.03 mol), and ammonium acetate (3.85 g, 0.05 mol) in ethanol (25 ml) was refluxed for 2 h, during which time yellowish orange crystals separated. The crystals were collected by filtration, washed with hot ethanol, then recrystallized from methanol / benzene to yield 6.3 g (95%) of **2**; mp 219-220 °C; ir (KBr) ν_{max} 3150, 2220, 1650 cm^{-1}; ^1H nmr ($CDCl_3$) δ 7.35 (d, *J* = 4.6 Hz, 1 H), 7.58 (t, *J* = 4.0 Hz, 1 H), 7.71 (t, *J*= 4.0 Hz, 1 H), 7.95 (d, *J* = 4.6 Hz, 1 H), 8.22 (d, *J* = 4.2 Hz, 1 H), 8.48 (d, J = 4.2 Hz, 1 H), 8.81 (s, 1 H), 9.19 (s, 1 H); ^{13}C nmr ($CDCl_3$) δ 103.77, 111.76, 116.10, 116.66, 122.703, 126.51, 129.40, 129.34, 129.34, 130.18, 135.92, 143.67, 152.23, 154.55. *Anal.* Calcd for $C_{14}H_8N_2O$: C, 76.35; H, 3.66; N, 12.72. Found: C, 76.12; H, 3.58; N, 12.72.

B. Preparation of 2-Amino-1-cyano-5-cyanomethyl-2*H*-benzo[*f*]chromano-[2,3,4:*d*,*e*]pyrido[2,3-*d*]pyrimidine (**3**). A mixture of malononitrile (4.96 g, 0.06 mol), 2-hydroxy-1-naphthaldehyde (**1**, 5.16 g, 0.03 mol), and ammonium acetate (3.85 g, 0.05 mol) in ethanol (25 ml) was treated in similar manner as that described above for the synthesis of **2** to yield 7.7 g (73%) of compound (**3**); yellow crystals, mp > 350 °C (dioxane); ir (KBr) ν_{max} 3450, 2220, 1650 cm^{-1}; ^1H nmr ($CDCl_3$) δ 5.01 (s, 2 H), 5.94 (s, 2 H), 7.58 (t, *J* = 4.0 Hz, 1 H), 7.71 (t, *J*= 4.0 Hz, 1 H), 7.95 (d, *J* = 4.6 Hz), 8.22 (d, *J* = 4.2 Hz, 1 H), 8.48 (d, J = 4.2 Hz, 1 H), 8.81 (s, 1 H),

9.19 (s, 1 H). *Anal.* Calcd for $C_{20}H_{10}N_6O$: C, 68.57; H, 2.88; N, 23.99. Found: C, 68.50; H, 3.00; N, 23.94.

Reaction of 1 and Malononitrile with Acetophenone. A. Reaction time of 2 h. A mixture of malononitrile (2.98 g, 0.03 mol), 2-hydroxy-1-naphthaldehyde (**1**, 5.16 g, 0.03 mol), acetophenone (3.6 g, 0.03 mol) and ammonium acetate (3.85 g, 0.05 mol) in ethanol (25 ml) was refluxed for 2 h, during which time dark crystals separated from the solution. The mixture was then cooled to room temperature, the crystals were collected by filtration then fractionally recrystallized using mixtures of benzene and methanol to obtain 1.05 g (10%) of compound (**3**) 1.56 g (18%) of 5-cyanomethyl-2-phenyl-2*H*-benzo[*f*]chromano[2,3,4:*d,e*]pyrido[2,3-*d*]pyrimidine (**4**), and 1.03 g, (12%) of 4-imino-2-cyanomethyl-2*H*-benzo[*f*]chromeno[2,3-*d*]pyrimidine (**5**).

Compound 4: yellow solid; mp 270-273 °C (benzene / methanol); ir (KBr) ν_{max} 2220, 1660 cm^{-1}; ^1H nmr (DMSO) δ 3.93 (s, 2 H), 6.36-6.45 (m, 1 H), 6.82-6.92 (m, 1 H), 7.02 (t, *J*= 4.0 Hz, 1 H), 7.20-8.38 (m, 10 H), 8.93 (s, 1 H). *Anal.* Calcd for $C_{25}H_{14}N_4O$: C, 77.71; H, 3.65; N, 14.50. Found: C, 77.60; H, 3.80; N, 14.67.

Compound 5: mp 230-231 °C; ir (KBr) ν_{max} 3150, 2220, 1650 cm^{-1}; ^1H nmr (DMSO) δ 3.95 (s, 2 H), 7.35 (d, *J* = 4.6 Hz, 1 H), 7.58 (t, *J* = 4.0 Hz, 1 H), 7.71 (t, *J*= 4.0 Hz, 1 H), 7.95 (d, *J* = 4.6 Hz, 1 H), 8.22 (d, *J* = 4.2 Hz, 1 H), 8.48 (d, J = 4.2 Hz, 1 H), 8.31 (s, 1 H). *Anal.* Calcd for $C_{17}H_{10}N_4O$: C, 71.32; H, 3.53; N, 19.57. Found: C, 70.93; H, 3.44; N, 19.65.

B. Reaction time of 10 min. A mixture of malononitrile (2.98 g, 0.03 mol), 2-hydroxy-1-naphthaldehyde (**1**, 5.16 g, 0.03 mol), acetophenone (3.6 g, 0.03 mol) and ammonium acetate (3.85 g, 0.05 mol) in ethanol (25 ml) was refluxed for 10 min and then worked up as described above in **A** to give 0.99 g (15%) of compound (**2**), 1.16 g (10%) of compound (**4**), and 0.60 g (7%) of compound (**5**).

Reaction of 2 with Malononitrile and Ketones. A mixture of **2** (6.60 g, 0.03 mol), malononitrile (1.98 g, 0.03 mol), appropriate ketone (0.03 mol) and ammonium acetate (3.85 g, 0.05 mol) in ethanol (25 ml) was refluxed for 2 h, during which time yellow crystals separated from the reaction mixture. The crystals were obtained by filtration and recrystallized from dioxane to give 1.76 g (15%) of compound (**5**), 3.15 g (30%) of 2-cyanomethylcyclopentano[*g*]-2*H*-benzo[*f*]chromano[2,3,4:*d,e*]pyrido[2,3-*d*]pyrimidine (**7**), and 3.8 g (35%) of cyclohexano[*g*]-2*H*-benzo[*f*]chromano[2,3,4:*d,e*]pyrido[2,3-*d*]pyrimidine (**8**).

5-Cyanomethylcyclopentano[*g*]-2*H*-benzo[*f*]chromano-[2,3,4:*d,e*]pyrido[2,3-*d*]-pyrimidine (**7**): yellow crystals, mp 190-191 °C (dioxane); ir (KBr) ν_{max} 2219, 1657 cm^{-1}; ^1H nmr (DMSO) δ 2.50-2.60 (m, 6 H), 3.40 (s, 2 H), 7.06 (d, *J* = 6.9 Hz, 1 H), 7.30 (t, *J* = 4.4 Hz, 1 H), 7.43

(t, J = 4.4 Hz, 1 H), 7.65 (d, J = 6.9 Hz, 1 H), 7.78 (d, J = 5.2 Hz, 1 H), 7.85 (d, J = 5.2 Hz, 1 H). *Anal.* Calcd for $C_{22}H_{14}N_4O$: C, 75.42; H, 4.03; N,15.99. Found: C, 74.80; H, 4.10; N, 15.88.

5-Cyanomethylcyclohexano[*g*]- 2*H*-benzo[*f*]chromano[2,3,4:*d*,*e*]pyrido[2,3-*d*]pyrimidine (**8**): yellow crystals, mp 310-312 °C (dioxane); ir (KBr), ν_{max} 2223, 1654 cm^{-1}; ^1H nmr (DMSO) δ 2.40-2.60 (m, 6 H), 3.30 (m, 4 H), 7.06 (d, J = 6.9 Hz, 1 H), 7.30 (t, J = 4.4, 1 H), 7.43 (t, J = 4.4 Hz, 1 H), 7.65 (d, J = 6.9 Hz, 1 H), 7.78 (d, J = 5.2 Hz, 1 H), 7.85 (d, J = 5.2 Hz, 1 H). *Anal.* Calcd for $C_{23}H_{14}N_4O$: C, 68.57; H, 2.88; N, 23.99. Found: C, 68.80; H, 2.70; N, 23.88.

Reaction of 1 with Cyanoacetamide and Ammonium Acetate. A mixture of cyanoacetamide (2.52 g, 0.03 mol), 2-hydroxy-1-naphthaldehyde (**1**, 5.16 g, 0.03 mol), and ammonium acetate (3.85 g, 0.05 mol) in ethanol (25 ml) was refluxed for 2 h and then worked up manner as described for the reaction of **1** with malononitrile and ammonium acetate to give 4.3 g (65%) of 3-cyanobenzo[*g*]-2-quinolone (**9**), yellow crystals, mp 235-236 °C (dioxane); ir (KBr) ν_{max} 3350, 2220, 1680 cm^{-1}; ^1H nmr (DMSO) δ 7.32-7.37 (m, 1 H), 7.54-7.80 (m, 3 H), 7.80 (br s, 0.5 H), 7.96 (d, J = 7.3 Hz, 1 H), 8.07 (t, J = 9.1 Hz, 1 H), 8.29-8.36 (m, 1 H), 8.56 (d, J = 7.3 Hz, 1 H), 8.87 (s, 0.5 H), 8.97 (s, 0.5 H), 9.65 (br s, 0.5 H), 9.69 (s, 1 H); ^{13}C nmr (DMSO) δ 110.70, 112.26, 116.69, 122.51, 126.85, 128.76, 129.07, 129.38, 129.96, 134.11, 137.14, 149.48, 154.99, 164.11. *Anal.* Calcd for $C_{14}H_8N_2O$: C, 76.35; H, 3.66; N, 12.72. Found: C, 76.41; H, 3.69; N, 12.91.

Reaction of 1 with Cyanoacetamide and Cyclopentanone. A. In the Presence of Ammounium Acetate. A mixture of cyanoacetamide (2.52 g, 0.03 mol), 2-hydroxy-1-naphthaldehyde (**1**, 5.16 g, 0.03 mol), cyclopentanone (2.52 g, 0.03 mol), and ammonium acetate (3.85 g, 0.05 mol) in ethanol (25 ml) was refluxed for 2 h and then worked up manner as described for the reaction of **1** with cyanoacetamide and ammonium acetate to give 5.57 g (78%) of 2-imino-2*H*-benzo[*f*]chromene-3-carboxamide (**10**), yellow crystals, mp 220-221 °C (dioxane); ^1H nmr ($CDCl_3$) δ 4.90 (bs, 2 H), 7.21 (d, J = 4.6 Hz, 1 H), 7.37 (t, J = 4.0 Hz, 1 H), 7.71 (t, J= 4.0 Hz, 1 H), 7.95 (d, J = 4.6 Hz, 1 H), 8.22 (d, J = 4.2 Hz, 1 H), 8.48 (d, J = 4.2 Hz, 1 H), 8.81 (s, 1 H), 9.81 (s, 1 H); ir (KBr) ν_{max} 3350, 2220, 1680 cm^{-1}. *Anal.* Calcd for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 76.30; H, 4.04; N, 11.83.

B. In the Presence of TEA. A mixture of cyanoacetamide (2.52 g, 0.03 mol), 2-hydroxy-1-naphthaldehyde (**1**, 5.16 g, 0.03 mol), cyclopentanone (2.52 g, 0.03 mol), and TEA (3.3 g, 0.05 mol) in ethanol (25 ml) was refluxed for 2 h and then worked up in same manner as described for the reaction of **1** with cyanoacetamide, cyclopentanone, and ammonium acetate to give 6.38

g (70%) of 5-aminocyclopentano[*b*]-4*H*-pyrano[4,3-*c*]-2-quinolone (**11**) and 7.47 g (82%) of 6-amino benzo[*f*]cyclopentano[*e*]-2-pyridono[3,4-*e*]chromene (**12**).

Preparation of Authentic Samples of 11 and 12. A mixture of Compound **9** (2.2 g, 0.01 mol) or **10** (2.38 g, 0.01 mol), cyclopentanone (0.83 g, 0.01 mol) and ammonium acetate (1.9 g, 0.25 mol) was refluxed in ethanol (25 ml) for 2 h during which yellow cyrstals appeared. The yellow crystals were obtained by filtration and recrystallized from dioxane to give 2.10 g (70%) of compound **11** or 2.49 g (82%) of compound **12**.

Compound **11**: mp 285-287 °C; ir (KBr) ν_{max} 3450, 3360, 1680, 1650 cm^{-1}; ^1H nmr (DMSO) δ 2.47 (m, 6 H), 7.39 (d, *J* = 8.8 Hz, 1 H), 7.60-7.71 (m, 2 H), 7.90-8.01 (m, 1 H), 8.36-8.42 (m, 1 H), 8.90 (s, 1 H), 9.02 (s, 1 H), 9.77 (s, 1 H). *Anal.* Calcd for $C_{19}H_{16}N_2O_2$: C, 75.98; H, 5.30; N, 9.20. Found: C, 76.03; H, 5.39; N, 9.31.

Compound **12**: mp 210-212 °C; ir (KBr) ν (cm^{-1}) 3450, 3360, 1680, 1650; ^1H nmr (DMSO) δ 2.47-2.51 (m, 6 H), 7.39 (d, J = 8.8 Hz, 1 H), 7.60-7.90 (m, 1 H), 7.90-8.01 (m, 1 H), 8.13 (d, J = 8.8 Hz, 1 H), 8.36-8.42 (m, 1 H), 8.90 (s, 1 H), 9.02 (s, 1 H), 9.64-9.66 (m, 0.5 H), 9.77 (s, 0.5 H). Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 75.98: H, 5.30; N, 9.20. Found: C, 76.20; H, 5.04; N, 9.29.

Reaction of 1, Cyanoacetamide and Ammonium Acetate with Various Ketones in Acetic Acid. A mixture of cyanoacetamide (2.52 g, 0.03 mol), 2-hydroxy-1-naphthaldehyde (**1**, 5.16 g, 0.03 mol), ammonium acetate (3.85 g, 0.05 mol), and 0.03 mol of either cyclopenta-none, isopropyl methyl ketone, or acetophenone in acetic acid (25 ml) was refluxed for 2 h, and the resulting yellow material recrystallized from dioxane to give 5.30 g (80%) of 3-cyanobenzo [*f*]chromen-2-one (**13**): mp 298-299 °C; ir (KBr) ν_{max} 2220, 1700 cm^{-1}; ^1H nmr (DMSO) δ 7.66 (m, 2 H), 7.78 (m, 1 H), 8.09 (d, J = 7.9 Hz, 1 H), 8.31 (d, *J* = 8.1 Hz, 1 H), 8.58 (d, *J* = 8.1 Hz, 1 H), 9.47 (s, 1 H); ^{13}C nmr δ 113.21, 116.89, 118.62, 122,77, 127.06, 129.20, 129.54, 129.55, 130.2, 136.2, 143.48, 155.90, 163.30, 172.50. *Anal.* Calcd for $C_{14}H_7NO_2$: C, 76.01; H, 3.19; N, 6.33. Found: C, 75.54; H, 3.13; N, 6.40.

Reaction of 2-Hydroxy-1-naphthaldehyde (1) and Ethyl Cyanoacetate in the presence of Ammonium Acetate. A mixture of 2-hydroxy-1-naphthaldehyde (**1**, 5.16 g, 0.03 mol), ammonium acetate (3.85 g, 0.05 mol), and ethyl cyanoacetate (3.45 g, 0.03 mol) was refluxed in acetic acid (25 ml) for 2 h, and the resulting yellow solid was recrystallized from dioxane to yield 13 g (64%) of 3-carbethoxy-2*H*-benzo[*f*]chromene (**14**), mp 242-243 °C; ir (KBr) ν_{max}1720, 1700 cm^{-1}; ^1H nmr (DMSO) δ 1.04 (t, *J* = 7.1 Hz, 3 H), 3.40 (q, *J* = 7.01 Hz, 2 H), 7.47 (d, *J* = 5.1 Hz, 1 H), 7.62 (m, 1 H), 7.67 (m, 1 H), 8.13 (d, *J* = 4.2 Hz, 1 H), 8.41 (d, *J* = 4.2 Hz, 1 H), 8.52 (d, *J* = 3.8 Hz, 1 H), 8.80 (d, *J* = 3.8 Hz, 1 H), 8.93 (*s*, 1 H), 9.60 (s, 1 H). *Anal.* Calcd for

$C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.04; H, 4.64; N, 5.37.

Reaction of 2-Hydroxy-1-naphthaldehyde (1), Ethyl Cyanoacetate, and Cyclopentanone in presence of Ammonium Acetate. A mixture of **1** (5.16 g, 0.03 mol), ammonium acetate (3.85 g, 0.05 mol), ethyl cyanoacetate (3.45 g, 0.03 mol), and cyclopentanone (2.46 g, 0.03 mol) in ethanol (25 ml) was refluxed for 2 h to yield 6.64 g (73%) of 5-iminobenzo[*f*]cyclopentano[*e*]-2*H*-pyranone[3,4-*c*]chromene (**15**);mp 278-279 °C (dioxane); ^{1}H nmr (DMSO) δ 2.49 (br s, 4 H), 3.33 (s, 2 H), 7.51 (d, *J* = 8.5, 1 H), 7.56-7.58 (m, 3 H), 8.04 (d, *J* = 7.9 Hz, 1 H), 8.18 (d, *J* = 8.5 Hz, 1 H). *Anal.* Calcd. for $C_{19}H_{15}NO_3$: C, 75.24; H, 4.32; N, 4.62. Found: C, 75.54; H, 4.44; N, 4.37.

Reaction of 1, Ethyl Cyanoacetate and Ammonium Acetate in Acetic Acid. 2-Carbethoxy-2*H*-benzo[*f*]-2-chromenone (16). A mixture of **1** (5.16 g, 0.03 mol), ammonium acetate (3.85 g, 0.05 mol), and ethyl cyanoacetate (3.45 g, 0.03 mol) in ethanol (25 ml) was refluxed for 2 h to yield 5.61g (70%) of 3-carbethoxy-2*H*-benzo[*f*]-2-chromenone (**16**, 5.61g, 70%), mp 118 °C ($CHCl_3$); ^{1}H nmr ($CDCl_3$) δ 1.46 (t, J = 7.2 Hz, 3 H), 4.48 (q, J = 7.2 Hz, 2 H), 7.47 (d, *J* = 5.1 Hz, 1 H), 7.62 (m, 1 H), 7.76 (m, 1 H), 7.86 (d, *J* = 4.2 Hz, 1 H), 8.11 (d, *J* = 4.2 Hz, 1 H), 8.11 (d, *J* = 3.8 Hz, 1 H), 8.23 (d, *J* = 3.8 Hz, 1 H), 9.23 (s, 1 H); ^{13}C nmr ($CDCl_3$) δ 14.3, 48.0, 62.1, 112.3, 116.5, 116.7, 121.5, 126.5, 129.1, 129.2, 129.4, 130.2, 136.1, 144.5, 155.96, 163.6. *Anal.* Calcd for $C_{16}H_{12}O_4$: C, 71.62; H, 4.50. Found: C, 75.29; H, 4.34.

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