Organic Preparations and Procedures International: The New Journal for Organic Synthesis
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uopp20

SYNTHESIS OF NOVEL BENZOCHROMENE, BENZOQUINOLINE, BENZOCHROMENOPYRIMIDINE AND PYRIMIDOBENZOQUINOLINE DERIVATIVES

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Published online: 11 Feb 2009.

To cite this article: M. N. Jachak , D. B. Kendre , A. B. Avhale , R. B. Toche & V. J. Medhane (2006) SYNTHESIS OF NOVEL BENZOCHROMENE, BENZOQUINOLINE, BENZOCHROMENOPYRIMIDINE AND PYRIMIDOBENZOQUINOLINE DERIVATIVES, Organic Preparations and Procedures International: The New Journal for Organic Synthesis, 38:3, 313-324

To link to this article: http://dx.doi.org/10.1080/00304940609355992

SYNTHESIS OF NOVEL BENZOCHROMENE, BENZOQUINOLINE, BENZOCHROMENOPYRIMIDINE AND PYRIMIDOBENZOQUINOLINE DERIVATIVES

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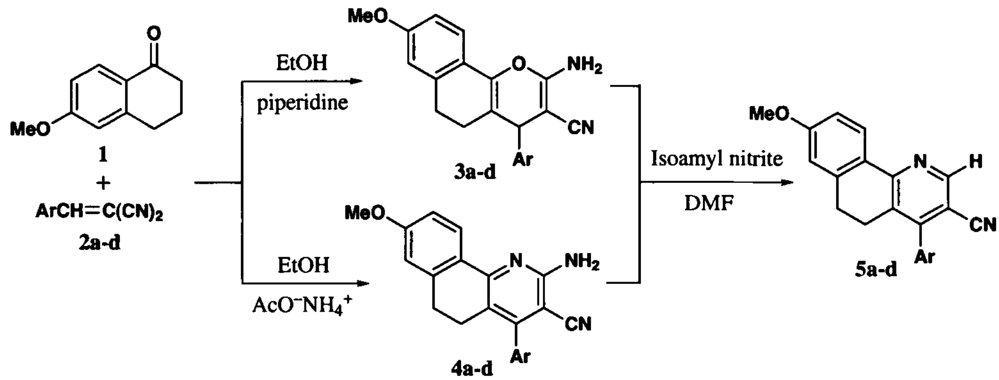
Benzochromene, benzoquinoline and their derivatives have a wide range of biological activities such as antimicrobial,[1,2] antiasthmic,[3] antimalarial,[4] antiseptic,[5] hypnotic, CNS and sedative activities.[6,7] These observations made it of interest to synthesize new tricyclic heterocycles which may have potential medicinal applications. The search for new heterocyclic compounds and for novel methods of their synthesis are major areas in contemporary organic chemistry.[8,9]

Otto and co-workers[5] had reported the synthesis of benzochromene and benzoquinoline derivatives by the Michael addition of malononitrile to 2-arylidene-1-tetralone. As part of our ongoing program in this area,[10,11] we now report the preparation of new tricyclic and tetracyclic heterocycles such as benzochromene, benzoquinoline, benzochromenopyrimidine and pyrimidobenzoquinoline derivatives from 6-methoxy-1-tetralone (**1**) by the Michael addition of benzylidenemalononitrile **2** to 6-methoxy-1-tetralone (**1**) in better yields and less time than by Otto's protocol.

Addition of 6-methoxy-1-tetralone (**1**) to benzylidenemalononitriles **2** in the presence of catalytic amount of piperidine in ethanol at reflux temperature yielded 2-amino-4-aryl-8-methoxy-5,6-dihydro-4*H*-benzo[*h*]chromene-3-carbonitriles **3** (*Scheme 1*) which were characterized by IR, PMR, ^{13}C NMR and elemental analysis. For example, **3a** showed absorptions at 3465, 3311, 2191 cm^{-1} in the IR spectrum which indicated the presence of NH_2 and CN groups respectively. The singlet at δ 4.06 and broad singlet at δ 4.53 confirmed the presence of C_4H and protons of NH_2 group respectively in ^{1}H NMR spectrum. The proposed structure of **3a** was further supported by ^{13}C NMR in $CDCl_3$ which exhibited peaks at δ 24, 28, 41, 55, 115 for C_5, C_6, C_4, OCH_3 and carbon of nitrile respectively and aromatic carbons were observed between δ 121-161. However, addition of compound **1** to benzylidenemalononitriles **2** in presence of ammonium acetate and catalytic amount of acetic acid in ethanol at reflux temperature yielded 2-amino-4-aryl-8-methoxy-5,6-dihydrobenzo[*h*]quinoline-3-carbonitriles **4** in good yield (*Scheme 1*). Structures of compounds **4** were assigned on the basis of spectroscopic and analytical data. For example, ^{13}C NMR in $CDCl_3$ of compound **4a** showed peaks at δ 24, 28, 56, 117 for C_5, C_6, OCH_3, and carbon of nitrile function respectively and aromatic carbons were observed between δ 126-159. Compounds **3** were used for the synthesis of benzochromenopyrimidines **7** as well as benzoquinolines **5** and **10**. Analogously, compounds **4** were used for the synthesis of benzo-quinolines **5** and pyrimidobenzoquinolines **9** (*Schemes 1-3*).

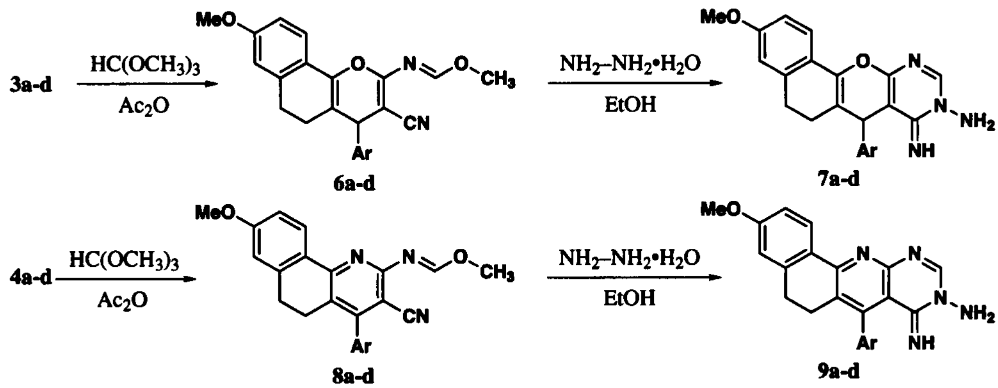


a) Ar = C_6H_5; b) Ar = *m*-ClC_6H_4; c) Ar = *m*-BrC_6H_4; d) Ar = *p*-ClC_6H_4

Scheme 1

The deamination of compounds **4** with isoamyl nitrite[12] in *DMF* yielded the benzoquinoline derivatives **5** (*Scheme 1*). The absence of NH_2 absorption band in the IR spectrum of **5a** and appearance of singlet at δ 7.83 for C_2H proton in ^1H NMR clearly confirmed its structure which was also supported by the ^{13}C NMR in $CDCl_3$, which showed peaks at δ 24, 28, 55, 119 for C_5, C_6, OCH_3 and carbon of the nitrile respectively and aromatic carbons were observed between δ 128-161. Similar reaction with compounds **3** unexpectedly yielded benzoquinolines **5** rather than the benzochromene. This may be due to opening of the pyran ring and cyclization to give the stable, fully aromatic benzoquinoline. Compounds **5** were characterized by IR, PMR, ^{13}C NMR and elemental analysis. Melting points, spectroscopic and analytical data of compounds **5** obtained either from **3** or **4** were identical.

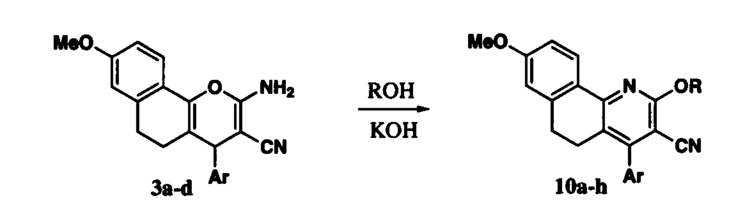
Treatment of benzochromenes **3** with trimethyl orthoformate in acetic anhydride at reflux yielded the benzo[*h*]chromen-2-ylimidoformates **6** which on cyclization with hydrazine hydrate in ethanol, led to benzochromenopyrimidines **7** in good yields. Compounds **6** and **7** were characterized by spectroscopic and analytical data. The NH_2 and NH stretching bands were observed at 3299, 3276, 3138 cm^{-1} in IR spectrum of **7a** and broad singlet at δ 5.54, 6.35 for NH_2 and NH protons in ^1H NMR spectrum respectively. This structural assignment was further supported by ^{13}C NMR in $CDCl_3$ which showed peaks at δ 24, 27, 42, 55 for C_6, C_7, C_5, OCH_3 respectively and aromatic carbons were observed between δ 127-159. A similar sequence of reactions was performed on the benzoquinoline derivatives **4**, which on treatment with trimethyl orthoformate in acetic anhydride at reflux temperature, yielded benzo[*h*]quinolin-2-ylimidoformates **8**; further treatment of **8** with hydrazine hydrate in ethanol at reflux temperature furnished pyrimidobenzoquinoline derivatives **9** (*Scheme 2*). Compounds **8** and **9** were characterized by IR, ^{1}H NMR and analytical data. The ^{13}C NMR in $CDCl_3$ of **9a** exhibit peaks at δ 24, 27, 53, for C_6, C_7, OCH_3 respectively and aromatic carbons between δ 128-160 also supported the proposed structure **9a**.



a) Ar = C_6H_5; b) Ar = *m*-ClC_6H_4; c) Ar = *m*-BrC_6H_4; d) Ar = *p*-ClC_6H_4

Scheme 2

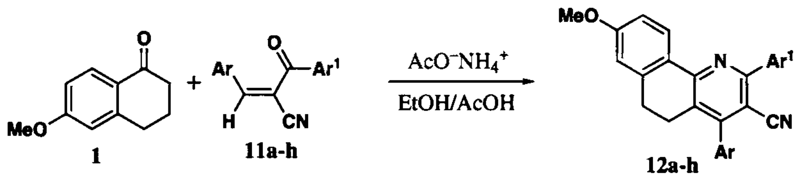
The benzochromenes **3** furnished the benzoquinoline derivatives **10a-d** upon reflux with methanolic potassium hydroxide. The corresponding ethyl ethers **10e-h** were obtained by treatment with ethanolic potassium hydroxide (*Scheme 3*). Formation of compounds **10** could arise from the attack of alkoxide ion on vinyl carbon, facilitated by the electron-withdrawing *o*-nitrile group and subsequent opening of the pyran ring followed by S_Ni attack of NH_2 to lead to the benzoquinoline derivatives.



a) R = Me, Ar = C_6H_5; b) R = Me, Ar = *m*-ClC_6H_4; c) R = Me, Ar = *m*-BrC_6H_4
d) R = Me, Ar = *p*-ClC_6H_4; e) R = Et, Ar = C_6H_5; f) R = Et, Ar = *m*-ClC_6H_4
g) R = Et, Ar = *m*-BrC_6H_4; h) R = Et, Ar = *p*-ClC_6H_4

The presence of C_2-OCH_3 in **10a** is indicated by a singlet at δ 4.19 in ^{1}H NMR spectrum and supported by peak at δ 54 in ^{13}C NMR spectrum. The presence of C_2-OCH_2CH_3 group in **10e** was confirmed by a triplet at δ 1.53 and quartet at δ 4.53 in ^{1}H NMR spectrum and peaks at δ 14, 62 and 126-162 for CH_3, OCH_2 and aromatic carbons respectively in ^{13}C NMR spectrum.

The condensation of 2-aroyl-3-arylacrylonitrile[13] **11** with 6-methoxy-1-tetralone (**1**) in presence of ammonium acetate and acetic acid in ethanol at reflux temperature furnished the benzoquinoline derivatives **12** which were characterized by spectroscopic and analytical data.



a) Ar, Ar_1 = C_6H_5; b) Ar = *m*-BrC_6H_4, Ar_1 = C_6H_5; c) Ar = *p*-ClC_6H_4, Ar_1 = C_6H_5
d) Ar = C_6H_5, Ar_1 = *p*-BrC_6H_4; e) Ar = *m*-ClC_6H_4, Ar_1 = *p*-BrC_6H_4; f) Ar = *p*-ClC_6H_4, Ar_1 = *p*-BrC_6H_4; g) Ar = C_6H_5, Ar_1 = *p*-ClC_6H_4; h) Ar = *m*-BrC_6H_4, Ar_1 = *p*-ClC_6H_4

Scheme 3

The ^{13}C NMR in $CDCl_3$ of **12a** exhibited peaks at δ 25, 27, 55,117 and 126-161 for C_5, C_6, OCH_3, CN and aromatic carbons respectively. The analytical and spectroscopic data for all above compounds are summarized in *Tables 1* and *2*.

Table 1. Yield, mps and Elemental Analysis of Compounds **3-12**

Cmpd.	Yield (%)	mp. (°C)	Elemental Analysis. (Found) C	H	N
3a	80	214-215	76.41 (76.22)	5.47 (5.25)	8.47 (8.30)
3b	82	220-222	69.13 (68.90)	4.69 (4.58)	7.67 (7.49)
3c	75	225-226	61.62 (61.40)	4.18 (4.00)	6.84 (6.90)
3d	72	190-192	69.13 (69.00)	4.69 (4.47)	7.67 (7.50)
4a	85	218-219	77.04 (76.90)	5.23 (5.16)	12.83 (12.60)
4b	90	211-213	69.70 (69.50)	4.45 (4.33)	11.61 (11.45)
4c	86	228-229	62.08 (61.90)	3.96 (3.74)	10.34 (10.20)
4d	88	207-208	69.70 (69.48)	4.45 (4.26)	11.61 (11.50)
5a	76	185-186	80.74 (80.55)	5.16 (5.05)	8.96 (8.76)
5b	70	195-196	72.72 (72.50)	4.35 (4.25)	8.07 (7.90)
5c	68	205-206	64.46 (64.23)	3.86 (3.74)	7.16 (6.97)
5d	73	190-192	72.72 (72.40)	4.35 (4.20)	8.07 (8.10)
6a	77	197-198	74.17 (74.00)	5.41 (5.21)	7.52 (7.43)
6b	60	207-209	67.89 (67.66)	4.70 (4.53)	6.88 (6.69)
6c	81	217-218	61.21 (61.01)	4.24 (4.12)	6.20 (6.00)
6d	71	181-183	67.89 (67.56)	4.70 (4.48)	6.88 (6.70)
7a	66	230-232	70.95 (70.79)	5.41 (5.21)	15.04 (15.00)
7b	69	225-227	64.94 (64.75)	4.70 (4.51)	13.77 (13.60)

Table 1. Continued...

Cmpd.	Yield (%)	mp. (°C)	Elemental Analysis. (Found) C	H	N
7c	78	235-237	58.54 (58.32)	4.24 (4.12)	12.41 (12.30)
7d	85	240-242	64.94 (64.74)	4.70 (4.49)	13.77 (13.55)
8a	77	205-206	74.78 (74.56)	5.18 (5.16)	11.37 (11.20)
8b	74	203-205	68.38 (68.26)	4.49 (4.46)	10.40 (10.23)
8c	80	219-220	61.62 (61.41)	4.04 (4.01)	9.37 (9.18)
8d	90	192-194	68.38 (68.16)	4.49 (4.26)	10.40 (10.27)
9a	79	230-232	71.52 (71.30)	5.18 (5.05)	18.98 (18.76)
9b	70	232-234	65.42 (65.28)	4.49 (4.37)	17.34 (17.20)
9c	75	240-241	58.94 (58.72)	4.04 (4.00)	15.62 (15.50)
9d	77	235-237	65.42 (65.20)	4.49 (4.27)	17.34 (17.21)
10a	81	185-187	76.95 (76.87)	5.28 (5.17)	8.18 (8.02)
10b	69	177-179	70.12 (69.99)	4.54 (4.46)	7.43 (7.22)
10c	77	187-189	62.72 (62.53)	4.06 (3.94)	6.64 (6.42)
10d	88	191-192	62.72 (62.53)	4.06 (3.94)	7.43 (7.20)
10e	91	167-168	77.56 (77.34)	5.63 (5.41)	7.86 (7.66)
10f	95	175-177	70.75 (70.53)	4.88 (4.53)	7.16 (7.00)
10g	96	188-186	63.54 (63.33)	4.38 (4.16)	6.43 (6.25)
10h	98	178-180	70.75 (70.50)	4.88 (4.66)	7.16 (7.02)
12a	88	215-216	83.48 (83.37)	5.18 (5.00)	7.21 (7.17)
12b	89	225-227	69.38 (69.27)	5.18 (4.21)	5.99 (5.80)
12c	78	201-203	76.68 (76.47)	5.18 (4.31)	6.62 (6.60)
12d	79	185-186	69.38 (69177)	4.00 (3.90)	5.99 (5.84)
12e	82	190-191	64.62 (64.50)	3.61 (3.38)	5.58 (5.51)
12f	86	198-200	64.62 (64.40)	3.61 (3.41)	5.58 (5.44)
12g	90	180-181	76.68 (76.47)	4.52 (4.30)	6.62 (6.60)
12h	94	191-192	64.62 (64.40)	3.61 (3.40)	5.58 (5.61)

a) All compounds are colorless solids

Table 2. Spectroscopy Data of Compounds **3-12**

Cmpd.	IR (cm^{-1})	^1H NMR (δ)
3a	3465, 3311, 2376, 2191, 1136,	2.02 (m, 2H, CH_2), 2.66 (m, 2H,CH_2), 3.81 (s, 3H, OCH_3), 4.06 (s, 1H,C_4H), 4.53 (s, 2H, NH_2), 6.68 (d, J = 2.8 Hz, $C_{10}H$), 6.74 (dd, J = 8.3, 2.8 Hz, C_9H), 7.28 (m, 5H, Ar-H), 7.37 (d, J = 8.3 Hz, C_7H)

Table 2. Continued...

Cmpd.	IR (cm^{-1})	^{1}H NMR (δ)
3b	3465, 3211, 2370, 2231, 1253,	1.98 (m, 2H, CH_2), 2.65 (m, 2H,CH_2), 3.81 (s, 3H, OCH_3), 4.05 (s, 1H,C_4H), 4.53 (s, 2H, NH_2), 6.69 (d, J = 2.8 Hz, $C_{10}H$), 6.75 (dd, J = 8.4, 2.8 Hz, C_9H), 7.18 (m, 4H, Ar-H), 7.37 (d, J = 8.4 Hz, C_7H)
3c	3365, 3211, 2241,1510, 1130,	2.01 (m, 2H, CH_2), 2.70 (m, 2H,CH_2), 3.84 (s, 3H, OCH_3), 4.64 (s, 1H,C_4H), 4.53 (s, 2H, NH_2), 6.71 (d, J = 2.7 Hz, $C_{10}H$), 6.72 (dd, J = 8.3, 2.7 Hz, C_9H), 7.19 (m, 4H, Ar-H), 7.40 (d, J = 8.3 Hz, C_7H)
3d	3398, 3223, 2237,1552, 1230,	2.03 (m, 2H, CH_2), 2.77 (m, 2H,CH_2), 3.86 (s, 3H, OCH_3), 4.12 (s, 1H,C_4H), 4.62 (s, 2H, NH_2), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 6.89 (dd, J = 8.4, 2.8 Hz, C_9H), 7.25 (m, 4H, Ar-H), 8.23 (d, J = 8.4 Hz, C_7H)
4a	3455, 3321, 2213, 1542, 1163,	2.59 (m, 2H, CH_2), 2.74 (m, 2H,CH_2), 3.85 (s, 3H, OCH_3), 5.40 (s, 2H, NH_2), 6.71 (d, J = 2.8 Hz, $C_{10}H$), 6.89 (dd, J = 8.4, 2.8 Hz, C_9H), 7.29 (m, 5H, Ar-H), 8.24 (d, J = 8.4 Hz, C_7H)
4b	3265, 3315, 2244, 1534, 1133,	2.59 (m, 2H, CH_2), 2.74 (m, 2H,CH_2), 3.86 (s, 3H, OCH_3), 5.15 (s, 2H, NH_2), 6.71 (d, J = 2.8 Hz, $C_{10}H$), 6.86 (dd, J = 8.4, 2.7 Hz, C_9H), 7.30 (m, 4H, Ar-H), 8.19 (d, J = 8.4 Hz, C_7H)
4c	3345, 3316, 2214, 1512, 1153,	2.59 (m, 2H, CH_2), 2.74 (m, 2H,CH_2), 3.85 (s, 3H, OCH_3), 5.15 (s, 2H, NH_2), 6.72 (d, J = 2.8 Hz, $C_{10}H$), 6.85 (dd, J = 8.4, 2.8 Hz, C_9H), 7.28 (m, 4H, Ar-H), 8.19 (d, J = 8.4 Hz, C_7H)
4d	3265, 3315, 2244, 1591, 1128,	2.59 (m, 2H, CH_2), 2.74 (m, 2H,CH_2), 3.85 (s, 3H, OCH_3), 5.15 (s, 2H, NH_2), 6.72 (d, J = 2.8 Hz, $C_{10}H$), 6.85 (dd, J = 8.4, 2.8 Hz, C_9H), 7.28 (m, 4H, Ar-H), 8.19 (d, J = 8.4 Hz, C_7H)
5a	2929, 2233, 1552, 1163,	2.90 (m, 2H, CH_2), 3.10 (m, 2H,CH_2), 3.88 (s, 3H, OCH_3), 6.70 (d, J = 2.8 Hz $C_{10}H$), 6.86 (dd, J = 8.4, 2.8 Hz, C_9H), 7.33 (m, 5H, Ar-H), 7.83 (s, 1H, C_2H) 8.24 (d, J = 8.4 Hz, C_7H)
5b	2925, 2228, 1546, 1145	2.91 (m, 2H, CH_2), 3.02 (m, 2H,CH_2), 3.84 (s, 3H, OCH_3), 6.70 (d, J = 2.7 Hz, $C_{10}H$), 6.86 (dd, J = 8.4, 2.7 Hz, C_9H), 7.23 (m, 4H, Ar-H), 7.81 (s, 1H, C_2H) 8.10 (d, J = 8.4 Hz, C_7H)
5c	2976, 2248, 1536, 1120	2.88 (m, 2H, CH_2), 2.90 (m, 2H,CH_2), 3.82 (s, 3H, OCH_3), 6.71 (d, J = 2.8 Hz, $C_{10}H$), 6.83 (dd, J = 8.4, 2.8 Hz, C_9H), 7.26 (m, 4H, Ar-H), 7.80 (s, 1H, C_2H) 8.10 (d, J = 8.4 Hz, C_7H)
5d	2915, 2228, 1526, 1256	2.91 (m, 2H, CH_2), 3.05 (m, 2H,CH_2), 3.81 (s, 3H, OCH_3), 6.70 (d, J = 2.8 Hz, $C_{10}H$), 6.83 (dd, J = 8.4, 2.8 Hz, C_9H), 7.28 (m, 4H, Ar-H), 7.81 (s, 1H, C_2H) 8.10 (d, J = 8.4 Hz, C_7H)

Table 2. Continued...

Cmpd.	IR (cm^{-1})	^1H NMR (δ)
6a	2325, 2214, 1569, 1160	1.73 (m, 2H, CH_2), 2.54 (m, 2H,CH_2), 3.70 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3) 4.27 (s, 1H,C_4H), 6.72 (s,1H, Ar-H), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 7.25 (m, 5H, Ar-H), 7.47 (d, J = 2.8 Hz, C_9H), 8.69 (s, 1H, N = CH)
6b	2356, 2230, 1453, 1520, 1166	1.73 (m, 2H, CH_2), 2.54 (m, 2H,CH_2), 3.70 (s, 3H, OCH_3), 3.83 (s, 3H,OCH_3) 4.33 (s, 1H,C_4H), 6.71 (s,1H, Ar-H), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 7.29 (m, 4H, Ar-H), 7.47 (d, J = 2.7 Hz, C_9H), 8.69 (s, 1H, N = CH)
6c	2371, 2232, 1512, 1157	1.73 (m, 2H, CH_2), 2.55 (m, 2H,CH_2), 3.71 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3) 4.32 (s, 1H,C_4H), 6.72 (s,1H, Ar-H), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 7.28 (m, 4H, Ar-H), 7.47 (d, J = 2.8 Hz, C_9H), 8.69 (s, 1H, N = CH)
6d	2344, 2230, 1596, 1145	1.73 (m, 2H, CH_2), 2.54 (m, 2H,CH_2), 3.70 (s, 3H, OCH_3), 3.84 (s, 3H,OCH_3), 6.70 (s, 1H, Ar-H), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 7.29 (m, 4H, Ar-H), 7.47 (d, J = 2.7 Hz, C_9H), 8.69 (s, 1H, N = CH)
7a	3299, 3276, 3138, 1554, 1132	1.81 (m, 2H, CH_2), 2.63 (m, 2H,CH_2), 3.67 (s, 3H, OCH_3), 4.36 (s, H, C_5H), 5.54 (s, 2H, NH_2), 6.35 (bs, 1H ,NH), 6.68 (d, J = 2.8 Hz, $C_{11}H$), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 7.11 (m, 6H, Ar-H), 7.97 (s, 1H, C_2H)
7b	3298, 3270, 3136, 1544, 1132	1.81 (m, 2H, CH_2), 2.61 (m, 2H,CH_2), 3.63 (s, 3H, OCH_3), 4.37 (s, H, C_5H), 5.52 (s, 2H, NH_2), 6.32 (bs, 1H, NH), 6.68 (d, J = 2.8 Hz, $C_{11}H$), 6.72 (d, J = 2.7 Hz, $C_{10}H$), 7.27 (m, 5H, Ar-H), 7.95 (s, 1H, C_2H)
7c	3299, 3276, 3144, 1542	1.81 (m, 2H, CH_2), 2.61 (m, 2H,CH_2), 3.63 (s, 3H, OCH_3), 4.37 (s, H, C_5H), 5.52 (s, 2H, NH_2), 6.32 (bs, 1H, NH), 6.68 (d, J = 2.8 Hz, $C_{11}H$), 6.72 (d, J = 2.8 Hz, $C_{10}H$), 7.27 (m, 5H, Ar-H), 7.95 (s, 1H, C_2H)
7d	3299, 3276, 3138, 1554	1.81 (m, 2H, CH_2), 2.62 (m, 2H,CH_2), 3.64 (s, 3H, OCH_3), 4.39 (s, H, C_5H), 5.53 (s, 2H, NH_2), 6.33 (bs, 1H, NH), 6.68 (d, J = 2.8 Hz, $C_{11}H$), 6.72 (d, J = 2.8 Hz, $C_{10}H$), 7.26 (m, 5H, Ar-H), 7.95 (s, 1H, C_2H)
8a	2344, 2224, 1520, 1176	1.72 (m, 2H, CH_2), 2.52 (m, 2H,CH_2), 3.71 (s, 3H, OCH_3), 3.83 (s, 3H,OCH_3) 6.72 (s, 1H, Ar-H), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 7.25 (m, 5H, Ar-H), 7.47 (d, J = 2.8 Hz, C_9H), 8.69 (s, 1H, N = CH)
8b	2412, 2231, 1596, 1144	1.70 (m, 2H, CH_2), 2.50 (m, 2H,CH_2), 3.74 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3) 6.72 (s, 1H, Ar-H), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 7.22 (m, 4H, Ar-H), 7.47 (d, J = 2.8 Hz, C_9H), 8.66 (s, 1H, N = CH)
8c	2355, 2237, 1605, 1145	1.74 (m, 2H, CH_2), 2.48 (m, 2H,CH_2), 3.69 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3) 6.71 (s, 1H, Ar-H), 6.76 (d, J = 2.8 Hz, $C_{10}H$), 7.22 (m, 4H, Ar-H), 7.47 (d, J = 2.8 Hz, C_9H), 8.67 (s, 1H, N = CH)

Table 2. Continued...

Cmpd.	IR (cm^{-1})	^{1}H NMR (δ)
8d	2376, 2241, 1526, 1114	1.70 (m, 2H, CH_2), 2.50 (m, 2H,CH_2), 3.74 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.72 (s, 1H, Ar-H), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 7.22 (m, 4H, Ar-H), 7.47 (d, J = 2.7 Hz, C_9H), 8.66 (s, 1H, N = CH)
9a	3288, 3276, 3126, 1526, 1132	1.81 (m, 2H, CH_2), 2.63 (m, 2H,CH_2), 3.67 (s, 3H, OCH_3), 5.54 (s, 2H, NH_2) 6.35 (bs, 1H, NH), 6.68 (d, J = 2.8 Hz, $C_{11}H$), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 7.11 (m, 6H, Ar- H), 7.97 (s, 1H, C_2H)
9b	3278, 3264, 3144, 1572	1.81 (m, 2H, CH_2), 2.61 (m, 2H,CH_2), 3.65 (s, 3H, OCH_3), 5.54 (s, 2H, NH_2), 6.35 (bs, 1H, NH), 6.67 (d, J = 2.7 Hz, $C_{11}H$), 6.74 (d, J = 2.7 Hz, $C_{10}H$), 7.11 (m, 5H, Ar- H), 7.97 (s, 1H, C_2H)
9c	3268, 3254, 3124, 1544	1.79 (m, 2H, CH_2), 2.58 (m, 2H,CH_2), 3.69 (s, 3H, OCH_3), 5.51 (s, 2H, NH_2), 6.35 (bs, 1H, NH), 6.67 (d, J = 2.8 Hz, $C_{11}H$), 6.74 (d, J = 2.8 Hz, $C_{10}H$), 7.11 (m, 5H, Ar- H), 7.97 (s, 1H, C_2H)
9d	3278, 3264, 3138, 1522	1.84 (m, 2H, CH_2), 2.64 (m, 2H,CH_2), 3.65 (s, 3H, OCH_3), 5.52 (s, 2H, NH_2) 6.33 (bs, 1H, NH), 6.73 (d, J = 2.8 Hz, $C_{11}H$), 6.74 (d, J = 2.7 Hz, $C_{10}H$), 7.11 (m, 5H, Ar- H), 7.97 (s, 1H, C_2H)
10a	2929, 2860, 2221, 1555, 844	2.67 (m, 2H, CH_2), 2.80 (m, 2H,CH_2), 3.90 (s, 3H, OCH_3), 419 (s, 3H, OCH_3), 6.67 (d, J = 2.8 Hz, $C_{10}H$), 6.93 (dd, J = 8.4, 2.8 Hz, C_9H), 7.29 (m, 5H, Ar-H), 8.30 (d, J = 8.3 Hz, C_7H)
10b	2929, 2858, 2214, 1550,1157, 862	2.63 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.90 (s, 3H, OCH_3), 420 (s, 3H, OCH_3), 6.77 (d, J = 2.7 Hz, $C_{10}H$), 6.92 (dd, J = 8.4, 2.7 Hz, C_9H), 7.24 (m, 4H, Ar-H), 8.26 (d, J = 8.3 Hz, C_7H)
10c	2923, 2858, 2214, 1550, 1157, 862	2.63 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.90 (s, 3H, OCH_3), 420 (s, 3H, OCH_3), 6.77 (d, J = 2.8 Hz, $C_{10}H$), 6.92 (dd, J = 8.4, 2.8 Hz, C_9H), 7.24 (m, 4H, Ar-H), 8.26 (d, J = 8.4 Hz, C_7H)
10d	2925, 2860, 2221, 1556, 1155, 844	2.66 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.90 (s, 3H, OCH_3), 419 (s, 3H, OCH_3), 6.77 (d, J = 2.7 Hz, $C_{10}H$), 6.93 (dd, J = 8.4, 2.7 Hz, C_9H), 7.21 (m, 4H, Ar-H), 8.30 (d, J = 8.4 Hz, C_7H)
10e	2221, 1600, 1552, 1157, 908, 846	1.53 (t, 3H, CH_3), 2.63 (m, 2H, CH_2), 2.81 (m, 2H, CH_2), 3.90 (s, 3H, OCH_3), 4.63 (q, 2H, OCH_2), 6.77 (d, J = 2.8 Hz, $C_{10}H$), 6.93 (dd, J = 8.4, 2.8 Hz, C_9H), 7.24 (m, 5H, Ar-H), 8.26 (d, J = 8.4 Hz, C_7H)
10f	2923, 2858, 2214, 1550, 1157, 862	1.51 (t, 3H, CH_3), 2.63 (m, 2H, CH_2), 2.81 (m, 2H, CH_2), 3.90 (s, 3H, OCH_3), 4.63 (q, 2H, OCH_2), 6.77 (d, J = 2.8 Hz, $C_{10}H$), 6.92 (dd, J = 8.4, 2.8 Hz, C_9H), 7.24 (m, 4H,Ar-H), 8.26 (d, J = 8.4 Hz, C_7H)

Table 2. Continued...

Cmpd.	IR (cm^{-1})	^1H NMR (δ)
10g	2922, 2858, 2216, 1550, 1157, 862	1.51 (t, 3H, CH_3), 2.62 (m, 2H, CH_2), 2.81 (m, 2H, CH_2), 3.91 (s, 3H, OCH_3), 4.61 (q, 2H, OCH_2), 6.66 (d, *J* = 2.7 Hz, $C_{10}H$), 6.91 (dd, *J* = 8.4, 2.7 Hz, C_9H), 7.22 (m, 4H,Ar-H), 8.27 (d, *J* = 8.4 Hz, C_7H)
10h	2218, 1602, 1427, 1161, 1028, 877	1.51 (t, 3H, CH_3), 2.64 (m, 2H, CH_2), 2.80 (m, 2H, CH_2), 3.90 (s, 3H, OCH_3), 4.63 (q, 2H, OCH_2), 6.67 (d, *J* = 2.8 Hz, $C_{10}H$), 6.92 (dd, *J* = 8.4, 2.8 Hz, C_9H), 7.28 (m, 4H,Ar-H), 8.26 (d, *J* = 8.4 Hz, C_7H)
12a	2929, 2215, 1542, 1153, 950	2.73 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.88 (s, 3H, OCH_3), 6.75 (d, *J* = 2.8 Hz, $C_{10}H$), 6.90 (dd, *J* = 8.4 2.7 Hz, C_9H), 7.24 (m, 10H,Ar-H), 8.39 (d, *J* = 8.4 Hz, C_7H)
12b	2929, 2219, 1542, 1163, 950	2.73 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.88 (s, 3H, OCH_3), 6.75 (d, *J* = 2.8 Hz, $C_{10}H$), 6.90 (dd, *J* = 8.4, 2.8 Hz, C_9H), 7.24 (m, 9H,Ar-H), 8.39 (d, *J* = 8.4 Hz, C_7H)
12c	2939, 2219, 1532, 1163, 950	2.73 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.88 (s, 3H, OCH_3), 6.75 (d, *J* = 2.8 Hz, $C_{10}H$), 6.90 (dd, *J* = 8.3, 2.8 Hz, C_9H), 7.24 (m, 9H,Ar-H), 8.39 (d, *J* = 8.3 Hz, C_7H)
12d	2939, 2219, 1542, 1163, 950	2.73 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.88 (s, 3H, OCH_3), 6.75 (d, *J* = 2.7 Hz, $C_{10}H$), 6.90 (dd, *J* = 8.4, 2.8 Hz, C_9H), 7.24 (m, 9H,Ar-H), 8.39 (d, *J* = 8.4 Hz, C_7H)
12e	2928, 2221, 1542, 1163, 950	2.73 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.88 (s, 3H, OCH_3), 6.75 (d, *J* = 2.8 Hz, $C_{10}H$), 6.90 (dd, *J* = 8.4, 2.8 Hz, C_9H), 7.24 (m, 9H, Ar-H), 8.39 (d, *J* = 8.4 Hz, C_7H)
12f	2928, 2221, 1542, 1163, 950	2.76 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.87 (s, 3H, OCH_3), 6.74 (d, *J* = 2.8 Hz, $C_{10}H$), 6.90 (dd, *J* = 8.4, 2.8 Hz, C_9H), 7.25 (m, 9H,Ar-H), 8.39 (d, *J* = 8.4 Hz, C_7H)
12g	2929, 2219, 1542, 1163, 950	2.73 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.88 (s, 3H, OCH_3), 6.75 (d, *J* = 2.8 Hz, $C_{10}H$), 6.90 (dd, *J* = 8.4, 2.8 Hz, C_9H), 7.24 (m, 9H,Ar-H), 8.39 (d, *J* = 8.4 Hz, C_7H)
12h	2917, 2235, 1532, 1163, 950	2.73 (m, 2H, CH_2), 2.81 (m, 2H,CH_2), 3.85 (s, 3H, OCH_3), 6.73 (d, *J* = 2.8 Hz, $C_{10}H$), 6.91 (dd, *J* = 8.4, 2.7 Hz, C_9H), 7.21 (m, 9H,Ar-H), 8.35 (d, *J* = 8.4 Hz, C_7H)

a) All compounds are colorless solids

EXPERIMENTAL SECTION

Melting points were determined on a Gallenkamp Melting point apparatus and are uncorrected. Elemental analysis was determined on a Hosli C, H Analyzer. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 MHz spectrometer using TMS as an internal standard. IR spectra were obtained as Nujol mulls on a Schimadzu IR 408 spectrometer.

2-Amino-8-methoxy-4-aryl-5,6-dihydro-4*H*-benzo[*h*]chromene-3-carbonitriles (3).

General Procedure.- A solution of **1** (1.76 g, 0.01 mole) and benzylidenemalononitrile **2** (1.54 g, 0.01 mole) in ethanol (15 mL) in presence of piperidine (0.5 mL) was refluxed for 5 hr. The solid formed on cooling was collected, washed with ethanol, dried and recrystallized from ethanol to yield **3a**. Compounds **3b-d** were prepared similarly and recrystallized from ethanol.

2-Amino-8-methoxy-4-aryl-5,6-dihydrobenzo[*h*]quinoline-3-carbonitriles (4).

General Procedure.- A solution of **1** (1.76 g, 0.01 mole), benzylidenemalononitrile **2** (1.54 g, 0.01 mole), ammonium acetate (1.54 g, 0.02 mole) and acetic acid (0.5 mL) in absolute ethanol (15 mL) was refluxed for 5 hr. The solid formed on cooling was collected, washed with ethanol, dried and recrystallized from ethanol to yield **4a**. Compounds **4b-d** were prepared similarly and were recrystallized from ethanol.

8-Methoxy-4-aryl-5, 6-dihydrobenzo[*h*]quinoline-3-carbonitriles (5).

General Procedure.- A solution of **3a** (3.30 g, 0.01 mole) or **4a** (3.27 g, 0.01 mole) and isoamyl nitrite (1.34 mL, 0.01 mole) in *DMF* (10 mL) was stirred at 90-95°C for 3 hr. The solvent was removed under reduced pressure, the solid obtained was collected and recrystallized from ethanol to yield **5a**. Compounds **5b-d** were synthesized similarly and were recrystallized from ethanol.

Methyl 3-cyano-8-methoxy-4-aryl-5,6-dihydro-4*H*-benzo[*h*]chromen-2-ylimidoformates (6).

General Procedure.- A solution of **3a** (3.30 g, 0.01 mole) and trimethyl orthoformate (1.09 mL, 0.01 mole) in acetic anhydride (15 mL) was refluxed for 1 hr. Then the solvent was removed under reduced pressure, the solid obtained was collected, washed with ethanol, dried and recrystallized from ethanol to yield **6a**. Compounds **6b-d** were obtained similarly and recrystallized from ethanol.

3 (5*H*)-Amine-4-imino-5-aryl-6,7-dihydro-9-methoxy-4*H*-benzochromeno[2,3-*d*]pyrimidines (7).

General Procedure.- A solution of **6a** (3.72 g, 0.01 mole) and hydrazine hydrate (0.48 mL, 0.01 mole) in absolute ethanol (15 mL) was refluxed for 1 hr. The solid formed was collected, washed with ethanol, dried and recrystallized from *DMF*-ethanol (1:2) to yield **7a**. Compounds **7b-d** were synthesized similarly and recrystallized from *DMF*-ethanol.

Methyl 3-cyano-8-methoxy-4-aryl-5,6-dihydrobenzo[*h*]quinolin-2-ylimidoformates (8).

General Procedure.- A solution of **4a** (3.27 g, 0.01 mole), trimethyl orthoformate (1.09 mL, 0.01 mole) in acetic anhydride (15 mL) was refluxed for 1 hr. Then the solvent was removed under reduced pressure, the solid obtained was collected, washed with ethanol, dried and recrystallized from ethanol to yield **8a**. Compounds **8b-d** were synthesized similarly and recrystallized from ethanol.

3 (4*H*)-Amine-4-imino-5-aryl-6,7-dihydro-9-methoxypyrimido[4,5-*b*]benzoquinolines (9).

General Procedure.- A solution of **8a** (3.69 g, 0.01 mole) and hydrazine hydrate (0.48 mL, 0.01 mole) in absolute ethanol (15 mL) was refluxed for 1 hr. The solid formed was collected, washed with ethanol, dried and recrystallized from *DMF*-ethanol (1:2) to yield **9a**. Compounds **9b-d** were obtained similarly and recrystallized from *DMF*-ethanol.

2, 8-Dimethoxy-4-aryl-5,6-dihydrobenzo[*h*]quinoline-3-carbonitriles (10).

General Procedure.- A solution of **3a** (3.30 g, 0.01 mole) in dry methanol (15 mL) catalytic amount of potassium hydroxide was added and refluxed for 45 minutes. The solid formed on cooling was collected, washed with methanol, dried and recrystallized from methanol to yield **10a**. Compounds **10b-d** were synthesized similarly and were recrystallized from methanol. Compounds **10e-h** were synthesized similarly by using ethanolic potassium hydroxide and recrystallized from ethanol.

2,4-Diarnyl-8-methoxy-5,6-dihydrobenzo[*h*]quinoline-3-carbonitriles (12).

General Procedure.- A solution of **1** (1.76 g, 0.01 mole) and 2-benzoyl-3-phenylacrylonitrile **11a** (2.33 g, 0.01 mole) in absolute ethanol (15 mL), ammonium acetate (1.54 g, 0.02 mole) and acetic acid (1 mL) were added and refluxed for 3 hr. The solid formed on cooling was collected, washed with ethanol, dried and recrystallized from ethanol to yield **12a**. Compounds **12b-h** were synthesized similarly and recrystallized from ethanol.

Acknowledgement.- The present work is supported by research project sanctioned by University Grants Commission, New Delhi. The authors thank Principal V. B. Gaikwad for providing facilities.

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(Received September 28, 2005; in final form March 14, 2006)