REACTION OF 3-IODOCHROMONE WITH NUCLEOPHILE 1. REACTION OF 3-IODOCHROMONE WITH AZOLES

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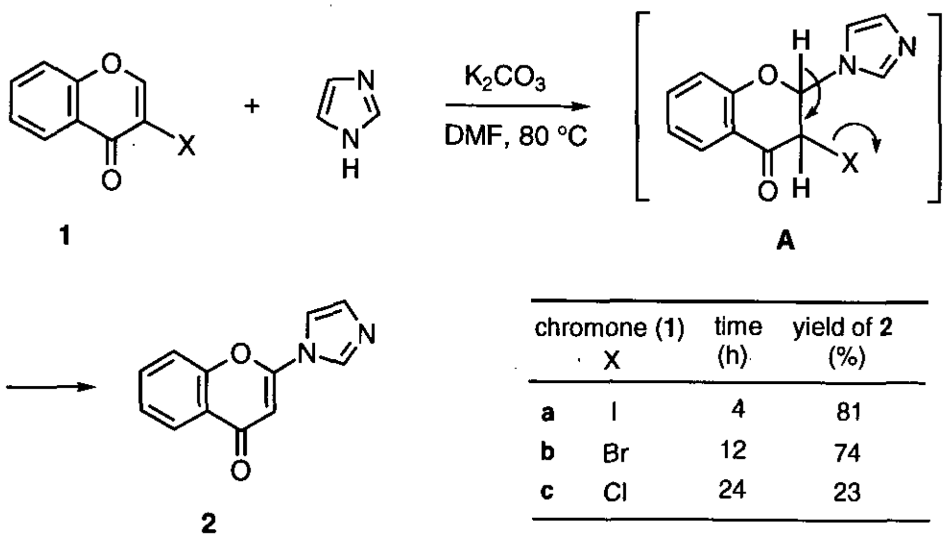
Abstract- 3-Iodochromone (**1a**) reacted with azoles, such as imidazole and pyrazole to afford 2-(*N*-azolyl)chromones (**2-7**) under very mild conditions in high yields. In the case of indoles as the nucleophile, aurone derivatives (**9**) were obtained together with 2-(*N*-indolyl)chromones (**8**).

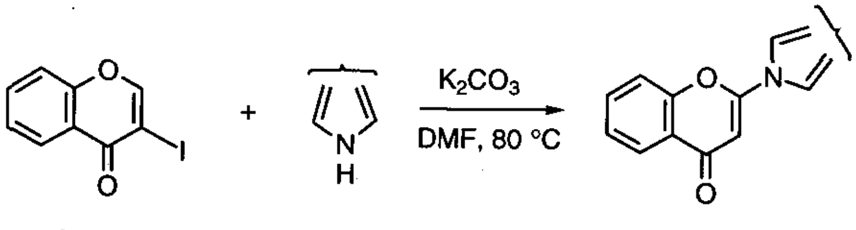
As 3-iodochromone (**1a**)[1] has an α,β-unsaturated carbonyl moiety and a good leaving group (I^-) at the 3-position of the pyrone ring, the conjugated addition reaction (Michael reaction) will be expected to occur at the 2-position of the chromone skeleton with a nucleophile. Several groups have shown some conjugated addition reactions of chromones having an electron withdrawing group at the 3-position with several nucleophiles such as lithium dialkylcuprate.[2] We report here the conjugated addition reaction of 3-iodochromone (**1a**) with azoles as the nucleophile. The treatment of 3-iodochromone (**1a**) with imidazole in the presence of potassium carbonate as a base in DMF while heating at 80 ℃ gives 2-(1-imidazolyl)chromone (**2**), mp 193 ℃, in 81% yield. The compound (**2**) showed a molecular ion peak at m/z 212 in its ms spectrum, and the pmr spectrum showed a proton signal at the 3-position of the chromone ring at 6.40 ppm. The ir spectrum of **2** showed a carbonyl absorption at 1640 cm^{-1} and no NH signal was observed. On the basis of these spectroscopic properties, the structure of this compound was determined as having a nitrogen atom at the 1-position of the imidazole was attached to the 2-position of the chromone ring. The reactivity of this reaction decreased when 3-bromo- or 3-chlorochromone was used instead of 3-iodochromone (Scheme 1).

The results of these reactions using the several azoles are summarized in Table 1. All of the reactions smoothly proceeded to give the corresponding chromone as the sole product in satisfactory yields. In these reactions, the first step may be the Michael type addition of the azole to the active site (2-position of the chromone ring) to afford intermediate (**A**) followed by the elimination of H-I to give 2-(*N*-azolyl)chromone.



chromone (1)	X	time (h)	yield of **2** (%)
a	I	4	81
b	Br	12	74
c	Cl	24	23

Scheme 1

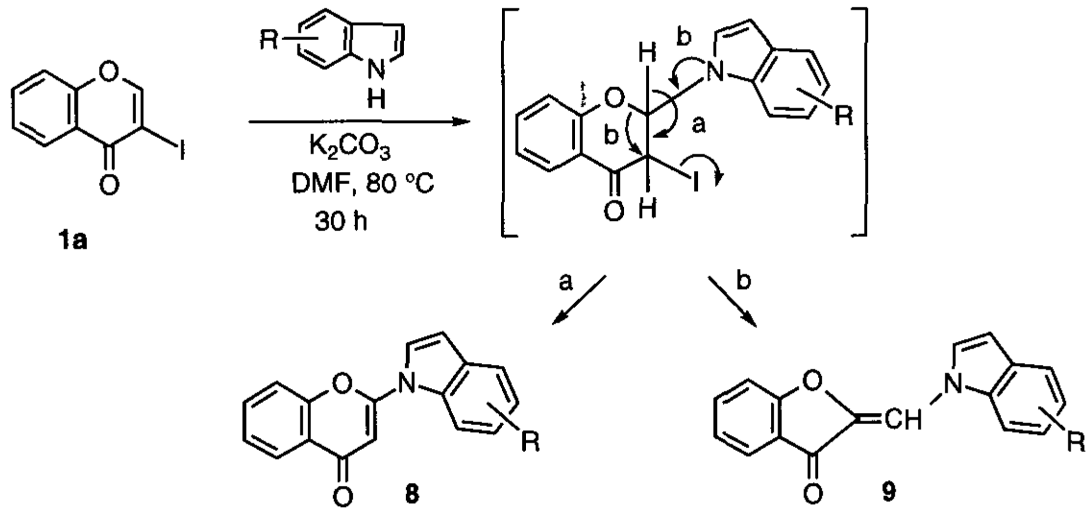


1a **2-7**

Table 1. Reaction of 3-iodochromone (**1a**) with azole derivatives

Entry	Azole	Reaction time (h)	Product No.	Yield (%)
1	imidazole	4	**2**	81
2	pyrazole	20	**3**	71
3	pyrrole	20	**4**	56
4	1,2,4-triazole	2	**5**	64
5	benzimidazole	2	**6**	87
6	indazole	30	**7**	89

Interestingly, the treatment of **1a** with indole as the nucleophile under the same conditions afforded the aurone derivative (**9a**) in 30% yield together with the normal product (**8a**) in 32% yield, respectively (Entry 1 in Table 3). It is obvious that the former product was formed by the rearrangement of the initially formed intermediate (**A**). Similarly, the reactions of **1a** with some substituted indoles were carried out under the same conditions and resulted in the formation of **8** and **9** as shown in Table 3. Substituents on the indole ring exerted a profound effect on the ratio of products. Namely, indoles bearing an electron-donating group (3-methyl, 5-methyl or 5-methoxy group) provided the increased ratio of **9**. On the contrary, **8** was obtained as the sole product and no aurone derivative (**9**) was detected, when the reactions with indole having a nitro group were carried out. Based on the these results, the typical reaction pathway for the reaction using indoles are illustrated as follow (Scheme 2).



Scheme 2

Thus, in the case of indoles, nitrogen atoms are more electron rich than the other azoles, and the **b** process may be partly accelerated to afford compound (**9**). These facts were in good agreement with the ir spectra data[3] of the *N*-acetylazoles (Table 2). Only *N*-acetylindole has an absorption of carbonyl frequencies below 1720 cm^{-1}.

Table 2.
Carbonyl frequencies for *N*-acetylazole

N-Acetylazole	ν (C=O) (cm^{-1})
pyrrole	1732
imidazole	1747
1,2,4-triazole	1765
indole	1711
benzimidazole	1729

P. Cozzi[4] reported the preparation of **2** by the reaction of 3-bromochromone (**1b**) and the silver salt of imidazole, but our present procedure is cheaper and good yields are obtained.

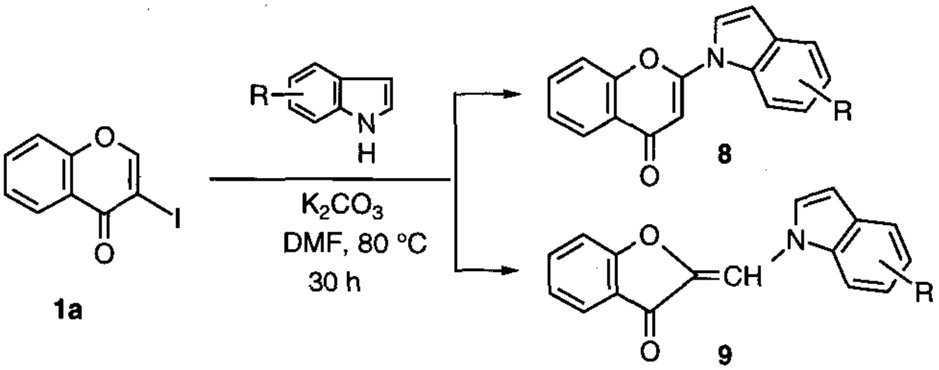


Table 3. Reaction of 3-iodochromone (**1a**) with indole derivatives

Entry	Indole R	Product No.	Yield (%)
1	H	**8a**	32
		9a	30
2	3-Me	**8b**	14
		9b	64
3	5-Me	**8c**	24
		9c	42
4	5-OMe	**8d**	23
		9d	30
5	5-Cl	**8e**	59
		9e	trace
6	5-NO_2	**8f**	58
		9f	0
7	6-NO_2	**8g**	78
		9g	0

In conclusion, this work provides a general synthesis for a variety of 2-(*N*-azolyl)chromones from 3-iodochromone with azoles under mild conditions, and revealed that 3-iodochromone is reactive to nucleophiles as expected.

EXPERIMENTAL

All melting points were determined using a Yanagimoto micro-hot stage and are uncorrected. Ir spectra were recorded using a JASCO IR-810 spectrophotometer and ^{1}H-nmr spectra were measured using a JEOL GX-270 spectrometer with tetramethylsilane as the internal standerd. Mass spectra were recorded using a JEOL DX-300 spectrometer. Uv spectra were obtained using a JASCO UVIDEC-430A spectrophotometer. Column chromatography was done on Wakogel (C-200).

General Procedure for Conjugated Addition Reaction of 3-Iodochromone (1a) with Azoles. A mixture of 3-iodochromone (**1a**) (1 mmol), azoles (2 mmol) and K_2CO_3 (10 mmol) in DMF (5 ml) was stirred for 2-30 h at 80 ℃. After removal of K_2CO_3, the reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. The residue was purified by silica gel column chromatography to give 2-azolylchromones (**2-7**). The yields are given in **Table 1**.

2-(1-Imidazolyl)-4*H*-benzopyran-4-one (2). mp 193 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1640 (C=O). Ms m/z: 212 (M$^+$). Uv λ_{max}^{MeOH} nm (log ε): 233 (4.28), 280 (4.19). ^{1}H-Nmr (CDCl$_3$) δ: 6.40 (1H, br. s, H-3), 7.28 (1H, m, H-4'), 7.46-7.58 (2H, m, H-6, 8), 7.48 (1H, m, H-5'), 7.76 (1H, t, J=7.9 Hz, H-7), 8.23 (1H, s, H-2'), 8.24 (1H, dd, J=8.1, 1.8 Hz, H-5). Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.80; H, 3.85; N, 13.18.

2-(1-Pyrazolyl)-4*H*-benzopyran-4-one (3). mp 143-144 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1640 (C=O). Ms m/z: 212 (M$^+$). Uv λ_{max}^{MeOH} nm (log ε): 240 (4.14), 294 (4.28). ^{1}H-Nmr (CDCl$_3$) δ: 6.59 (1H, dd, J=2.3, 1.8 Hz, H-4'), 6.90 (1H, s, H-3), 7.46-7.58 (2H, m, H-6, 8), 7.76 (1H, t, J=7.8 Hz, H-7), 7.85 (1H, d, J=1.8 Hz, H-3'), 8.23 (1H, d, J=2.3 Hz, H-5'), 8.24 (1H, dd, J=8.1, 1.8 Hz, H-5). Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.90; H, 3.85; N,13.22.

2-(1-Pyrrolyl)-4*H*-benzopyran-4-one (4). mp 134-135 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1640 (C=O). Ms m/z: 211 (M$^+$). Uv λ_{max}^{MeOH} nm (log ε): 238 (4.19), 300 (4.32). ^{1}H-Nmr (CDCl$_3$) δ: 6.31 (1H, s, H-3), 6.44 (2H, br. t, H-3', 4'), 7.32 (2H, br. t, H-2', 5'), 7.41-7.54 (2H, m, H-6, 8), 7.70 (1H, t, J=7.8 Hz, H-7), 8.22 (1H, dd, J=8.1, 1.8 Hz, H-5). Anal. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.30; N, 6.63. Found: C, 74.02; H, 4.42; N, 6.60.

2-[1-(1,2,4-Triazolyl)]-4*H*-benzopyran-4-one (5). mp 210 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1640 (C=O). Ms m/z: 213 (M$^+$). Uv λ_{max}^{MeOH} nm (log ε): 242 (4.13), 276 (4.20). ^{1}H-Nmr (CDCl$_3$) δ: 6.90

(1H, s, H-3), 7.47-7.60 (2H, m, H-6, 8), 7.77 (1H, t, J=7.5 Hz, H-7), 8.19 (1H, s, H-3'), 8.26 (1H, dd, J=8.1, 1.8 Hz, H-5), 8.91 (1H, s, H-5'). Anal. Calcd for $C_{11}H_7N_3O_2$: C, 61.97; H, 3.31; N, 19.71. Found: C, 61.92; H, 3.40; N, 19.80.

2-(1-Benzimidazolyl)-4*H*-benzopyran-4-one (6). mp 232 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1650 (C=O). Ms m/z: 262 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 242 (4.13), 268 (4.10), 302 (4.28). ^{1}H-Nmr ($CDCl_3$) δ: 6.59 (1H, s, H-3), 7.45-7.50 (2H, m, H-5', 6'), 7.48-7.64 (2H, m, H-6, 8), 7.78 (1H, t, J=7.9 Hz, H-7), 7.86-7.94 (2H, m, H-4', 7'), 8.28 (1H, dd, J=8.1, 1.8 Hz, H-5), 8.48 (1H, s, H-2'). Anal. Calcd for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.32; H, 3.84; N, 10.76.

2-(1-Indazolyl)-4*H*-benzopyran-4-one (7). mp 237-238 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1640 (C=O). Ms m/z: 262 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 236 (4.33), 324 (4.36), 334 (4.43). ^{1}H-Nmr ($CDCl_3$) δ: 6.94 (1H, s, H-3), 7.35-7.53 (2H, m, H-5', 6'), 7.58-7.68 (2H, m, H-6, 8), 7.75 (1H, t, J=7.7 Hz, H-7), 7.82 (1H, m, H-4'), 8.26 (1H, m, H-7'), 8.26 (1H, dd, J=8.1, 1.8 Hz, H-5), 8.30 (1H, s, H-3'). Anal. Calcd for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.18; H, 3.88; N, 10.70.

General Procedure for Conjugated Addition Reaction of 3-Iodochromone (1a) with Indoles. Following the procedure given for preparation of **2**, 3-iodochromone (**1a**) and indoles were treated with K_2CO_3 in DMF at 80 ℃ for 30 h to give **8** and **9**.

Reaction of 3-Iodochromone with Indole. According to the general procedure, **1a** and indole were treated with K_2CO_3 to give **8a** and **9a** in 32% and 30% yields, respectively.

2-(1-Indolyl)-4*H*-benzopyran-4-one (8a). mp 157-158 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1630 (C=O). Ms m/z: 261 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 242 (4.34), 328 (4.24). ^{1}H-Nmr ($CDCl_3$) δ: 6.46 (1H, s, H-3), 6.80 (1H, d, J=3.7 Hz, H-3'), 7.28-7.42 (2H, m, H-5', 6'), 7.47 (1H, t, J=7.5 Hz, H-6), 7.55 (1H, d, J=3.7 Hz, H-2'), 7.58 (1H, d, J=8.4 Hz, H-8), 7.66 (1H, d, J=8.2 Hz, H-4'), 7.72 (1H, t, J=7.5 Hz, H-7), 7.99 (1H, d, J=8.2 Hz, H-7'), 8.26 (1H, dd, J=7.9, 1.7 Hz, H-5). Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 78.28; H, 4.28; N, 5.28.

2-(1-Indolyl)methylene-3(2*H*)-benzofuranone (9a). mp 207 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1640 (C=O). Ms m/z: 261 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 255 (4.17), 267 (4.15), 327 (3.90), 404 (4.11). ^{1}H-Nmr ($CDCl_3$) δ: 6.84 (1H, d, J=3.7 Hz, H-3'), 7.21-7.41 (4H, m, H-5, 7, 5', 6'), 7.61-7.70 (3H, m, H-6, 4', 7'), 7.81 (1H, s, =CH), 7.84 (1H, dd, J=7.7, 1.1 Hz, H-4), 8.18 (1H, d, J=3.7 Hz, H-2'). Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 78.30; H, 4.28; N, 5.34.

Reaction of 3-Iodochromone with 3-Methylindole. According to the general procedure, **1a** and 3-methylindole were treated with K_2CO_3 to give **8b** and **9b** in 14% and 64% yields, respectively.

2-[1-(3-Methylindolyl)]-4*H*-benzopyran-4-one (8b). mp 170-172 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1610 (C=O). Ms m/z: 275 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 242 (4.36), 334 (4.43). ^{1}H-Nmr ($CDCl_3$) δ: 2.37 (3H, s, Me), 6.39 (1H, s, H-3), 7.30-7.50 (2H, m, H-6, 8), 7.30-7.63 (4H, m, H-2', 4', 5', 6'), 7.32 (1H, t, J=7.7 Hz, H-7), 8.01 (1H, d, J=8.1 Hz, H-7'), 8.26 (1H, dd, J=8.1, 1.8 Hz, H-5). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.22; H, 4.82; N, 5.14.

2-[1-(3-Methylindolyl)]methylene-3(2*H*)-benzofuranone (9b). mp 219-220 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1630 (C=O). Ms m/z: 275 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 256 (4.20), 280 (4.16), 328 (3.70), 412 (4.41). ^{1}H-Nmr ($CDCl_3$) δ: 2.39 (3H, s, Me), 7.21-7.41 (4H, m, H-5, 7, 5', 6'), 7.54-7.69 (3H, m, H-6, 4', 7'), 7.77 (1H, s, =CH), 7.84 (1H, dd, J=8.1, 1.1 Hz, H-4), 7.96 (1H, s, H-2'). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.48; H, 4.84; N, 5.00.

Reaction of 3-Iodochromone with 5-Methylindole. According to the general procedure, **1a** and 5-methylindole were treated with K_2CO_3 to give **8c** and **9c** in 24% and 42% yields, respectively.

2-[1-(5-Methylindolyl)]-4*H*-benzopyran-4-one (8c). mp 184-186 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1620 (C=O). Ms m/z: 275 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 244 (4.31), 334 (4.40). ^{1}H-Nmr ($CDCl_3$) δ: 2.47 (3H, s, Me), 6.50 (1H, s, H-3), 6.73 (1H, d, J=4.0 Hz, H-3'), 7.20 (1H, dd, J=8.6, 2.2 Hz, H-6'), 7.45 (1H, d, J=2.2 Hz, H-4'), 7.45-7.60 (2H, m, H-6, 8), 7.53 (1H, d, J=4.0 Hz, H-2'), 7.73 (1H, t, J=7.7 Hz, H-7), 7.89 (1H, d, J=8.6 Hz, H-7'), 8.25 (1H, dd, J=7.6, 1.1 Hz, H-5). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.62; H, 4.82; N, 5.16.

2-[1-(5-Methylindolyl)]methylene-3(2*H*)-benzofuranone (9c). mp 205 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1640 (C=O). Ms m/z: 275 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 260 (4.22), 270 (4.24), 332 (3.75), 408 (4.48). ^{1}H-Nmr ($CDCl_3$) δ: 2.47 (3H, s, Me), 6.67 (1H, d, J=3.6 Hz, H-3'), 7.15-7.28 (2H, m, H-5, 7), 7.34 (1H, d, J=8.4 Hz, H-6'), 7.41 (1H, s, H-4'), 7.55 (1H, d, J=8.4 Hz, H-7'), 7.65 (1H, t, J=7.9 Hz, H-6), 7.77 (1H, s, =CH), 7.84 (1H, dd, J=7.7, 1.4 Hz, H-4), 8.14 (1H, d, J=3.6 Hz, H-2'). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.30; H, 4.84; N, 5.14.

Reaction of 3-Iodochromone with 5-Methoxyindole. According to the general procedure, **1a** and 5-methoxyindole were treated with K_2CO_3 to give **8d** and **9d** in 23% and 30% yields, respectively.

2-[1-(5-Methoxyindolyl)]-4*H*-benzopyran-4-one (8d). mp 179-180 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1640 (C=O). Ms m/z: 291 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 246 (4.31), 294 (4.12), 338 (4.45). ^{1}H-

Nmr ($CDCl_3$) δ: 3.89 (3H, s, OMe), 6.42 (1H, s, H-3), 6.74 (1H, d, J=3.7 Hz, H-3'), 7.00 (1H, dd, J=9.2, 2.6 Hz, H-6'), 7.11 (1H, d, J=2.6 Hz, H-4'), 7.47 (1H, t, J=7.5 Hz, H-6), 7.53 (1H, d, J=3.7 Hz, H-2'), 7.58 (1H, dd, J=8.4, 0.7 Hz, H-8), 7.72 (1H, t, J=7.9 Hz, H-7), 7.91 (1H, d, J=9.2 Hz, H-7'), 8.26 (1H, dd, J=8.1, 1.5 Hz, H-5). Anal. Calcd for $C_{18}H_{13}NO_3$: C, 74.21; H, 4.50; N, 4.81. Found: C, 74.20; H, 4.54; N, 4.82.

2-[1-(5-Methoxyindolyl)]methylene-3(2*H*)-benzofuranone (9d). mp 222-223 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1640 (C=O). Ms m/z: 291 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 266 (4.19), 274 (4.23), 336 (3.75), 410 (4.45). ^{1}H-Nmr ($CDCl_3$) δ: 3.87 (3H, s, OMe), 6.76 (1H, d, J=3.5 Hz, H-3'), 6.98 (1H, dd, J=9.2, 2.3 Hz, H-6'), 7.08 (1H, d, J=2.3 Hz, H-4'), 7.20-7.38 (2H, m, H-5, 7), 7.54 (1H,d, J=9.2 Hz, H-7'), 7.65 (1H, t, J=7.8 Hz, H-6), 7.72 (1H, s, =CH), 7.83 (1H, dd, J=8.1, 1.5 Hz, H-4), 8.14 (1H,d, J=3.5 Hz, H-2'). Anal. Calcd for $C_{18}H_{13}NO_3$: C, 74.21; H, 4.50; N, 4.81. Found: C, 74.40; H, 4.62; N, 4.88.

Reaction of 3-Iodochromone with 5-Chloroindole. According to the general procedure, **1a** and 5-chloroindole were treated with K_2CO_3 to give **8e** in 59% yield.

2-[1-(5-Chloroindolyl)]-4*H*-benzopyran-4-one (8e). mp 234-236 ℃ (benzene-hexane). Ir (KBr, cm^{-1}): 1640 (C=O). Ms m/z: 295 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 242 (4.42), 286 (4.19), 328 (4.45). ^{1}H-Nmr ($CDCl_3$) δ: 6.49 (1H, s, H-3), 6.88 (1H, d, J=3.7 Hz, H-3'), 7.33-7.55 (2H, m, H-6, 8), 7.60-7.82 (3H, m, H-7, 4', 6'), 7.73 (1H, d, J=3.7 Hz, H-2'), 7.98 (1H, d, J=8.8 Hz, H-7'), 8.20 (1H, dd, J=8.4, 1.5 Hz, H-5). Anal. Calcd for $C_{17}H_{10}NO_2Cl$: C, 69.04; H, 3.41; N, 4.74. Found: C, 68.98; H, 3.48; N, 4.68.

Reaction of 3-Iodochromone with 5-Nitroindole. According to the general procedure, **1a** and 5-nitroindole were treated with K_2CO_3 to give **8f** in 58% yield.

2-[1-(5-Nitroindolyl)]-4*H*-benzopyran-4-one (8f). mp >300 ℃ (DMF). Ir (KBr, cm^{-1}): 1660 (C=O). Ms m/z: 306 (M^+). Uv λ_{max}^{MeOH} nm (log ε): 244 (4.24), 302 (4.31), 430sh (4.10). ^{1}H-Nmr (DMSO-d_6) δ: 6.82 (1H, s, H-3), 7.17 (1H, d, J=4.0 Hz, H-3'), 7.52 (1H, t, J=7.7 Hz, H-6), 7.86-7.96 (2H, m, H-7, 8), 8.10 (1H, dd, J=8.1, 1.1 Hz, H-5), 8.23 (1H, dd, J=9.2, 2.2 Hz, H-6'), 8.28 (1H, d, J=4.0 Hz, H-2'), 8.38 (1H, d, J=9.2 Hz, H-7'). 8.67 (1H, d, J=2.2 Hz, H-4'). Anal. Calcd for $C_{17}H_{10}N_2O_4$: C, 66.66; H, 3.29; N, 9.15. Found: C, 66.72; H, 3.34; N, 9.18.

Reaction of 3-Iodochromone with 6-Nitroindole. According to the general procedure, **1a** and 6-nitroindole were treated with K_2CO_3 to give **8g** in 78% yield.

2-[1-(6-Nitroindolyl)]-4*H*-benzopyran-4-one (8g). mp 240 °C (MeOH). Ir (KBr, cm^{-1}): 1660 (C=O). Ms m/z: 306 (M$^+$). Uv λ_{max}^{MeOH} nm (log ε): 234 (4.36), 298 (4.38), 346 (4.12). ^{1}H-Nmr (DMSO-d_6) δ: 6.48 (1H, s, H-3), 6.94 (1H, d, J=3.7 Hz, H-3'), 7.53 (1H, t, J=7.7 Hz, H-6), 7.67 (1H, d, J=8.4 Hz, H-8), 7.74-7.84 (2H, m, H-7, 4'), 7.79 (1H, d, J=3.7 Hz, H-2'), 8.21 (1H, dd, J=8.4, 1.8 Hz, H-5'), 8.28 (1H, dd, J=8.1, 1.8 Hz, H-5), 8.97 (1H, d, J=1.8 Hz, H-7'). Anal. Calcd for $C_{17}H_{10}N_2O_4$: C, 66.66; H, 3.29; N, 9.15. Found: C, 66.50; H, 3.36; N, 9.20.

REFERENCES

1. R. B. Gammill, *Synthesis*, **1979**, 901.
2. S. T. Saengchantara and T. W. Wallace, *Tetrahedron*, 1990, **46**, 3029; P. D. Clarke, A. O. Fitton, H. Suschitzky, T. W. Wallace, H. A. Dowlatshahi, and J. L. Suschitzky, *Tetrahedron Lett.*, 1986, **27**, 91; T. W. Wallace, *Tetrahedron Lett.*, 1984, **25**, 4299; G. A. Caplin, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc.*, B, **1968**, 2302.
3. A. R. Katritzky and J. M. Lagwski, *Comprehensive Heterocyclic Chemistry*, vol. 5, Chapter 4.01, ed. by A. R. Katritzky and C. W. Rees, Pergamon Press, New York, 1984, p. 27.
4. P. Cozzi and A. Pillan, *J. Heterocycl. Chem.*, 1985, **22**, 441.

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