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3-(BENZIMIDAZOLYL-2)-2-IMINOCOUMARINS IN REACTIONS WITH AROMATIC ALDEHYDES

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Interaction of 3-(benzimidazolyl-2)-2-iminocoumarins with aromatic aldehydes in the presence of piperidine gave the corresponding 7-aryl-7H-benzo[4,5]imidazo[1,2-c]benzopyrano[3,2-e]pyrimidines. The 3-diethylamino derivatives of this series fluoresce effectively in alcohol solutions.

Keywords: 7-aryl-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidines, aromatic aldehydes, 3-(benzimidazolyl-2)-2-iminocoumarins, piperidine, fluorescence.

The spectral-luminescent properties of derivatives of 3-(benzimidazolyl-2)-2-iminocoumarins **1** have attracted the interest of investigators recently [1]. With the objective of modifying the structures of these compounds we have investigated their reactions with aromatic aldehydes **2**. It is known that similar reactions may lead to different compounds [2, 3]. We have observed that when 3-(benzimidazolyl-2)-2-iminocoumarins **1a-c** reacted with an excess of aromatic aldehydes **2a-d** in the presence of a catalytic amount of piperidine, only 7-aryl-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidines **3a-d** are formed in good yields.

The rate of the reaction depends considerably on the nature of the substituents of the iminocoumarin ring and the aldehyde. 7-Diethylamino-2-iminocoumarin (**1c**) reacts most readily with 5-methoxysalicylaldehyde (**2c**). In this case the reaction is complete after refluxing for 30 min in propanol to give compound **3d**. The formation of compounds **3b** and **3c** from coumarin **1c** and *p*-chlorobenzaldehyde (**2a**) and anisaldehyde **2b** respectively required a reaction time of 6 h. The reaction of compound **1a** with aldehyde **2d** to give compound **3a** required 36 h refluxing in butanol. Similar reactions occur with aliphatic aldehydes, but the corresponding products were almost never isolated in a pure state. Similarly the reaction of 2-iminocoumarins **1a** and **1c** with *p*-nitrobenzaldehyde **2f** and *p*-bromobenzaldehyde **2e** respectively led only to hydrolysis of the imino group (Scheme 1).

Ethanol solutions of compounds **3b-d**, containing the 3-diethylamino group, fluoresce at λ_{max} 502 (**3b**), 501 (**3c**), and 505 nm (**3d**) with quantum yields of fluorescence close to 100%. In the electronic absorption spectra of these compounds the longwave band shows well expressed vibrational structure. In the ^{1}H NMR spectra of compounds **3b-d** the singlet of the methyne proton at position 7 (7.3 ppm) is clearly shown only for compound **3d**. In the other compounds it is overlapped by the multiplet of the aromatic protons.

So the synthesized 7-aryl-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidines, containing the 3-NEt$_2$ group are of interest for further study as luminescent dyes.

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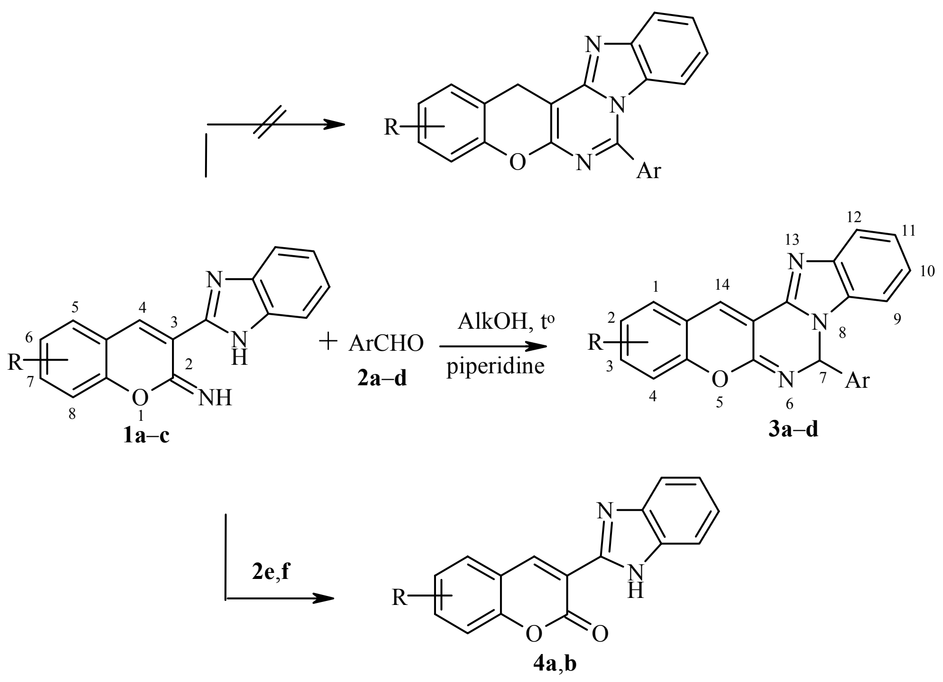
Scheme 1



1 **a** R = H; **b** R = 6-MeO; **c** R = 7-NEt$_2$; **2** **a** Ar = *p*-ClC$_6$H$_4$; **b** Ar = *p*-MeOC$_6$H$_4$;
c Ar = 2-OH-5-MeOC$_6$H$_3$; **d** Ar = *p*-Me$_2$NC$_6$H$_4$; **e** Ar = *p*-BrC$_6$H$_4$; **f** Ar = *p*-NO$_2$C$_6$H$_4$;
3 **a** R = H; **b–d** R = 3-NEt$_2$; **a** Ar = *p*-Me$_2$NC$_6$H$_4$; **b** Ar = *p*-ClC$_6$H$_4$; **c** Ar = *p*-MeOC$_6$H$_4$;
d Ar = 2-OH-5-MeOC$_6$H$_3$; **4** **a** R = H; **b** R = 6-MeO

EXPERIMENTAL

Electronic absorption spectra were measured with Hitachi U-3210 spectrophotometer, fluorescence spectra with a Hitachi U-4010 spectrophotometer. IR spectra of KBr tablets were recorded with a Specord IE-75 spectrometer. ^{1}H NMR spectra were recorded on a Varian Mercury 200 (200 MHz) in DMSO-d$_6$ with TMS as internal standard. Purity of all compounds was monitored by TLC on Silufol 200×200 mm sheets with 1:2 ethyl acetate–toluene as eluent.

TABLE 1. Reaction Times, Constants, and Yields of Compounds **3a-d**

Compound	Empirical formula	Found N, % Calculated N, %	mp, °C	Reaction time, h	Yield, %
3a	$C_{25}H_{20}N_4O$	14.35 14.28	269-270	36	80
3b	$C_{27}H_{23}ClN_4O$	12.26 12.31	276-278	6	65
3c	$C_{28}H_{26}N_4O_2$	12.34 12.44	260-261	6	60
3d	$C_{28}H_{26}N_4O_3$	12.10 12.01	271-272	0.5	85

TABLE 2. Spectral Characteristics of Compounds **3a-d**

Compound	UV spectrum, λ_{max}, nm, (ε)	IR spectrum, ν, cm^{-1}			^1H NMR spectrum, δ, ppm
		C=C	C=N	C–H	
3a	213 (57000), 255 (23300), 385 (24500)	1600, 1616	1668	2804, 2884, 3056	8.3 (1H, s,14-H); 7.8-7.6 (2H, m, 1-, 10-H); 7.5 (1H, t, 11-H); 7.3-7.0 (8H, m, 2-, 3-, 4-, 7-, 9-, 12-H, 2-, 6-H_{Ar}); 6.6 (2H, d, 3-, 5-Ar); 2.8 (6H, s, NMe_2)
3b	217 (56000), 295 (11700), 443 (57500)	1608	1676	2876, 2932, 3056	8.1 (1H, s, 14-H); 7.6 (1H, d, 12-H); 7.5 (1H, d, 9-H); 7.4-7.3 (5H, m, 1-, 7-, 10-H, 2-, 6-H_{Ar}); 7.2 (1H, m, 11-H); 7.1 (2H, d, 3-, 5-H_{Ar}); 6.6 (1H, d, 2-H); 6.5 (1H, s, 4-H); 3.4 (4H, q, $N(\underline{CH_2}CH_3)_2$); 1.1 (6H, t, $N(CH_2\underline{CH_3})_2$)
3c	218 (55100), 297 (11200), 444 (58000)	1624	1676	2840, 2972, 3056	8.1 (1H, s, 14-H); 7.6 (1H, d, 12-H); 7.5 (1H, d, 9-H); 7.3-7.0 (6H, m, 1-, 7-, 10-, 11-H, 2-, 6-H_{Ar}); 6.9 (2H, d, 3-, 5-H_{Ar}); 6.6 (1H, d, 2-H); 6.4 (1H, s, 4-H); 3.7 (3H, s, OMe); 3.4 (4H, q, $N(\underline{CH_2}CH_3)_2$); 1.1 (6H, t, $N(CH_2\underline{CH_3})_2$)
3d	213 (53100), 298 (14000), 440 (51000)	1608, 1628	1676	2876, 2976	9.3 (1H, s, OH); 8.1 (1H, s, 14-H); 7.6 (1H, d, 12-H); 7.5 (1H, d, 9-H); 7.3 (1H, s, 7-H); 7.2-7.0 (3H, m, 1-, 10-, 11-H); 6.8-6.6 (3H, m, 3-, 4-, 6-H_{Ar}); 6.6 (1H, d, 2-H); 6.4 (1H, s, 4-H); 3.6 (3H, s, OMe); 3.4 (4H, q, $N(\underline{CH_2}CH_3)_2$); 1.1 (6H, t, $N(CH_2\underline{CH_3})_2$)

7-Aryl-7H-benzo[4,5]imidazo[1,2-*c*]benzopyrano[3,2-*e*]pyrimidines (3a-d). (General Method). An aromatic aldehyde (3 mmol) was added to a solution of a 3-(benzimidazolyl-2)-2-iminocoumarin **1a-c** (2 mmol) in the minimum amount of boiling propanol or butanol, and boiling was continued for the time recorded in Table 1. The mixture was cooled, the precipitate was filtered off and recrystallized from butanol.

Physico-chemical and spectral characteristics are given in Tables 1 and 2.

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