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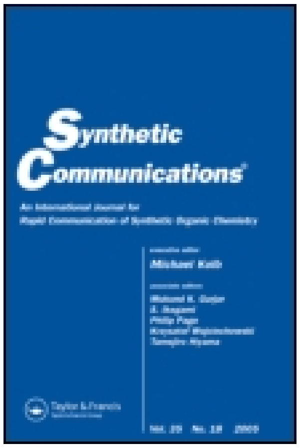

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Synthesis of New *bis*-Iminocoumarins by Schmidt Reaction Catalyzed by Ion-Exchange Resins

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ABSTRACT

A new synthetic route to *bis*-iminocoumarins is proposed which involves the synthesis of iminocoumarins from reaction of 2-hydroxybenzaldehydes with arylacetonitriles and their coupling with aromatic diamines. Ion-exchange resins were used as catalysts in both steps of this synthesis. The reaction parameters were varied and obtained using Amberlyst 15 resin in cyclohexane at 80°C.

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Key Words: *bis*-Iminocoumarins; Iminocoumarins; Diamine.

The synthesis of coumarin and iminocoumarin compounds has attracted much interest of their photophysical properties[1] and their biological activity.[2,3] In contrast to the extensive work reported on large number of coumarins, the work on the iminocoumarins and their derivatives is scanty, probably because of their high sensitivity of the hydrolyze when used homogenous catalysts. The use of ion-exchange resins as catalysts is not only for interest from their advantage to prevent this undesirable hydrolysis reaction, but offers considerable synthetic advantages in terms of yield, selectivity, and simplicity of the reaction procedure. Recently we reported the synthesis of several coumarin compounds obtained by Knoevenagel reaction catalyzed by IRA 900 resin in good yield and high selectivity.[4–6] The pursuit of this investigation based on the use of ion-exchange resins as catalysts led us to examine the possibility of preparing *bis*-iminocoumarins. To the best of our knowledge, this family of coumarin derivatives has been the subject of only one report which described the spectroscopic and laser properties of some bifluorophoric molecules obtained by linking coumarin and iminocoumarin moieties with thiazolyl cycle as a bridge.[7] However, the mechanism of the reaction, the process, and the detail structures of the products were not tackled in this work.

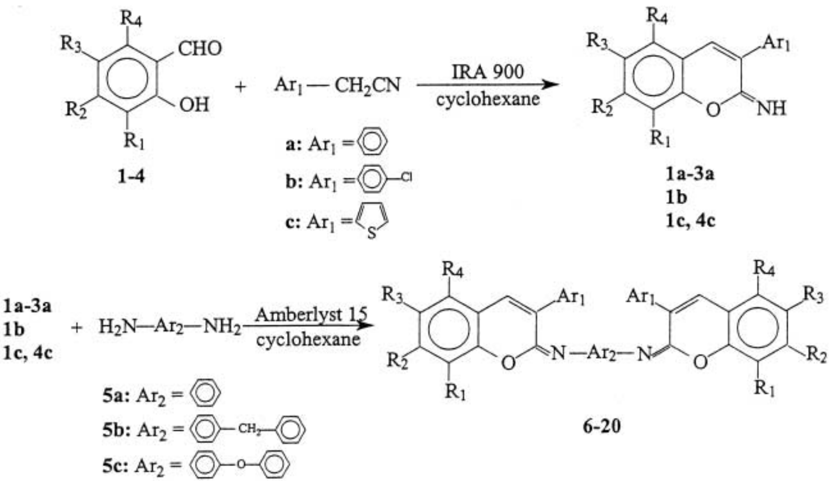
In this report we describe a novel and versatile method for synthesis of new bifluorophoric molecules incorporating two iminocoumarin nuclei. This method involved the synthesis of several iminocoumarins by Knoevenagel[8] reaction and their coupling with aromatic diamines by Schmidt reaction.

RESULTS AND DISCUSSION

The global reaction scheme leading to *N*,*N*′-arylene *bis*(3,3′-aryliminocoumarins) **6–20** is shown in Sch. 1.

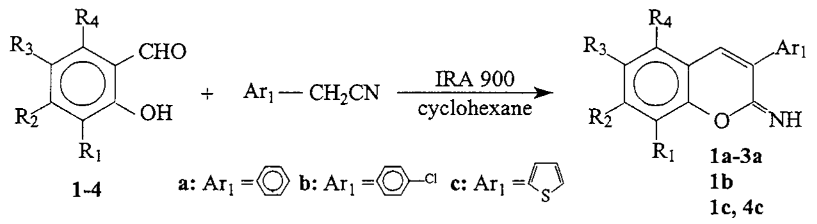
The reaction of aldehydes **1–4** with arylacetonitrile **a–c** in presence of basic resin Amberlite IRA 900 afford corresponding 3-aryliminocoumarins in good yield (Table 1). Their structures were assigned by IR, ^{1}H NMR, and ^{13}C NMR spectra.

In our approach to study the synthesis of *bis*-iminocoumarins **6–20** using Schmidt reaction in heterogeneous medium, we first concentrated on a model system **1a/5a** in order to evaluate the best synthetic conditions



Scheme 1.

Table 1. Synthesized of the substituted iminocoumarins **1a–3a**, **1b**, **1c**, and **4c**.



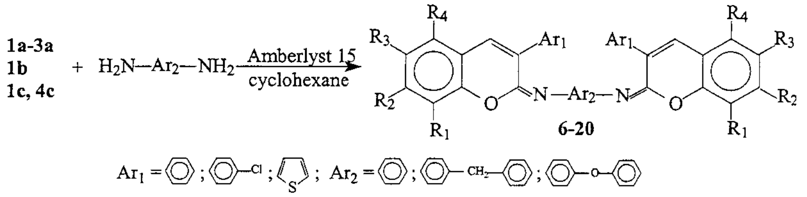
	R_1	R_2	R_3	R_4	Yield[a] (%)	Time (h)
1a	H	H	H	H	82	8
2a	H	H	Cl	H	50	10
3a	H	OMe	H	OMe	25	36
1b	H	H	H	H	72	4
1c	H	H	H	H	69	8
4c	H	OMe	H	H	61	8

[a] Isolated yield.

and then extended the study to other iminocoumarins and different diamines. Four parameters were varied in this context, namely the reaction temperature, the nature of the organic solvent, the nature of the catalyst, and its hydratation state.

The best yield of the desired compound **6** was obtained when Amberlyst 15 resin was utilized as a catalyst in cyclohexane at 80°C. Different experiments carried out with various hydratation states of the exchange resin led to a considerable variation in both yield and selectivity. In the present context we found that the best conditions for the formation of *bis*-iminocoumarins **6** required the use of Amberlyst 15 resin with 50 mg water/g of dry resin. The increase of resin hydratation state led to a decrease in yield of **6** and favorized the transformation of **1a** to corresponding coumarin by hydrolysis reaction. Following this successful synthesis several substituted *bis*-iminocoumarins were prepared (Table 2).

Table 2. Synthesized of the *N*,*N*′-arylene *bis*(3,3′-aryliminocoumarins) **6–20**.



				R_1	R_2	R_3	R_4	Yield[a] (%)	Time (h)
6	**1a**	+	**5a**	H	H	H	H	70	1
7	**2a**	+	**5a**	H	H	Cl	H	68	0.5
8	**3a**	+	**5a**	H	OMe	H	OMe	70	2
9	**1b**	+	**5a**	H	H	H	H	57	2
10	**1a**	+	**5b**	H	H	H	H	36	2
11	**2a**	+	**5b**	H	H	Cl	H	42	3
12	**3a**	+	**5b**	H	OMe	H	OMe	45	4
13	**1b**	+	**5b**	H	H	H	H	38	3
14	**1a**	+	**5c**	H	H	H	H	29	2
15	**2a**	+	**5c**	H	H	Cl	H	38	3
16	**1b**	+	**5c**	H	H	H	H	31	4
17	**1c**	+	**5a**	H	H	H	H	75	0.5
18	**1c**	+	**5b**	H	H	H	H	75	2
19	**4c**	+	**5b**	H	OMe	H	H	43	4
20	**1c**	+	**5c**	H	H	H	H	55	2

[a] Isolated yield.

CONCLUSION

New heterocyclic compounds containing two iminocoumarin nuclei have been synthesized and characterized. The process developed in this investigation is particularly interesting for its simplicity and for the advantage of providing this family of coumarin compounds in good yield and high selectivity.

Experimental Section

Aldehydes **1–4**, nitriles **a–c**, and diamines **5a–5c** are commercial products. Solvents (toluene and cyclohexane) were purified by standard techniques and redistilled prior to their use. Catalysts (IRA 900, A 15) were conditioned then used. Melting points were taken using a Electrothermal 9100 apparatus. IR spectra were obtained on a Jasco FT-IR 420 spectrophotometer apparatus (in KBr pellets). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker WP 200 spectrometer at 200.0 MHz and 50.32 MHz respectively, in $CDCl_3$ or DMSO-d_6, with TMS as internal standard (chemical shifts in ppm).

General Procedure for the Synthesis of 3-Aryliminocoumarins 1a–3a, 1b, 1c, and 4c

A mixture of aldehydes **1–4** (30 mmol), IRA 900 resin (3 g, 30 mmol OH^{-}), and cyclohexane (25 mL) are introduced in a 250 mL three-neck flask equipped with a condenser and stirred for 3 h at 80°C under a nitrogen atmosphere. After that, the arylacetonitriles **a–c** (30 mmol) were added and the mixture was refluxed for an appropriate time (Table 1). After completion of the reaction, the mixture was separated from the solid catalyst and the organic phase was concentrated under reduced pressure. The solid phase was purified by crystallizing with the hexane to give 3-aryliminocoumarins as a colorless solid.

3-Phenyliminocoumarin (1a): IR (KBr) [cm^{-1}]: $\nu = 3275$, 3050, 1644, 1594, 1063. ^{1}H NMR ($CDCl_3$) [ppm]: $\delta = 7.02–815$ (m, 11H, Ar_1). ^{13}C NMR ($CDCl_3$) [ppm]: $\delta = 116.1$, 119.3, 121.0, 123.6, 125.8, 127.9, 128.2, 128.9, 129.2, 129.4, 132.4, 138.6, 156.9. M.p. [°C] = 105.

6-Chloro,3-phenyliminocoumarin (2a): IR (KBr) [cm^{-1}]: $\nu = 3272$, 3041, 1644, 1590, 1052. ^{1}H NMR ($CDCl_3$) [ppm]: $\delta = 7.02–7.62$ (m, 8H, Ar_1), 7.82 (s, 1H, H4). ^{13}C NMR ($CDCl_3$) [ppm]: $\delta = 116.4$, 117.0, 117.3, 126.6, 128.3, 128.6, 129.2, 129.9, 130.6, 131.4, 132.1, 136.0, 152.0. M.p. [°C] = 128.

5,7-Dimethoxy,3-phenyliminocoumarin (3a): IR (KBr) [cm^{-1}]: $\nu = 3276$, 3057, 1648, 1611, 1065. ^{1}H NMR ($CDCl_3$) [ppm]: $\delta = 3.80$, 3.82 (2s, 6H, R_2–R_4), 6.15 (d, 1H, H6), 6.29 (d, 1H, H8), 7.43 (s, 1H, H4), 7.33–7.54 (m, 5H, Ar_1). ^{13}C NMR ($CDCl_3$) [ppm]: $\delta = 55.6$, 55.7, 92.4, 93.7, 103.0, 125.0, 128.1, 128.4, 128.6, 136.9, 154.0, 156.7, 162.5. M.p. [°C] = 150.

3-*p*-Chlorophenyliminocoumarin (1b): IR (KBr) [cm^{-1}]: $\nu = 3282$, 3069, 1649, 1596, 1067. ^{1}H NMR ($CDCl_3$) [ppm]: $\delta = 7.06$–7.16 (m, 4H, Ar_1), 7.36 (s, 1H, H4), 7.30–7.61 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) [ppm]: $\delta = 114.9$, 115.9, 123.3, 127.3, 128.2, 129.9, 130.3, 133.5, 134.0, 135.0, 153.0, 156.1. M.p. [°C] = 106.

3-(2-Thiophenyl)iminocoumarin (1c): IR (KBr) [cm^{-1}]: $\nu = 3276$, 3099, 1649, 1594, 1027. ^{1}H NMR ($CDCl_3$) [ppm]: $\delta = 7.04$–7.12 (m, 2H, H6–H7), 7.28 (2dd, 2H, H5–H8), 7.41 (s, 1H, H4), 7.10, 7.36, 7.66 (m, 3H, $Ar)_2$. ^{13}C NMR ($CDCl_3$) [ppm]: $\delta = 115.3$, 119.8, 123.7, 127.0, 127.2, 127.5, 127.6, 130.4, 130.9, 137.3, 152.6. M.p. [°C] = 80.

7-Methoxy-3-(2-thiophenyl)iminocoumarin (4c): IR (KBr) [cm^{-1}]: $\nu = 3295$, 3086, 1658, 1606, 1021. ^{1}H NMR ($CDCl_3$) [ppm]: $\delta = 3.83$ (s, 3H, R_2), 6.68 (dd, 1H, H6), 7.07 (d, 1H, H8), 7.24 (d, 1H, H5), 7.40 (s, 1H, H4), 6.64, 7.34, 7.59 (m, 3H, Ar_2). ^{13}C NMR ($CDCl_3$) [ppm]: $\delta = 56.1$, 94.0, 100.7, 111.3, 114.0, 126.8, 127.1, 127.5, 128.8, 132.0, 138.0, 156.0. M.p. [°C] = 90.

Table 3. Selected spectroscopic data for *N*,*N*′-arylene *bis*(3,3′-aryliminocoumarins) **6–20**.

	M.p. (°C)	IR/ν in cm^{-1}	^{1}H NMR/δ in ppm ($CDCl_3$) or (DMSO-d_6)[a]			
			MeO	CH_2	H_4	Ar_1–Ar_2
6[a]	>300	1637, 1593				7.21–7.99
7	240	1632, 1593			7.17	7.23–7.43
8	260	1634, 1588	3.78–3.85		7.55	6.36–7.78
9	>300	1627, 1585				7.05–7.75
10[a]	219	1645, 1595		4.02	7.67	7.16–7.35
11	182	1644, 1592		3.99	7.17	7.15–7.48
12	248	1644, 1591	3.78–3.85	3.96	7.56	7.15–7.76
13[a]	>300	1643, 1595		4.01		7.14–7.91
14[a]	>300	1645, 1599			7.67	7.12–7.87
15	185	1641, 1594			7.16	7.02–7.48
16	200	1643, 1599				6.99–7.80
17	260	1644, 1591			7.67	7.12–7.82
18	200	1646, 1595		4.01	7.60	7.09–7.74
19	165	1652, 1599	3.84	4.02	7.55	6.58–7.69
20	204	1645, 1606			7.63	7.38–7.76

General Procedure for the Synthesis of *N*,*N*′-Arylene *bis*(3,3′-Aryliminocoumarins) 6–20

To a stirred mixture of A 15 resin (3 g, 30 mmol H^+) and cyclohexane or toluene (25 mL) in 250 mL three-neck flask equipped with a condenser were added the 3-aryliminocoumarins (30 mmol). The mixture was refluxed for 3 h under a nitrogen atmosphere. Then diamines **5a–5c** (15 mmol) were added and the mixture was refluxed for an appropriate time (Table 3). The separated organic layer was evaporated from solvent and purified by crystallizing with the appropriate solvent to give *N*,*N*′-arylene *bis*(3,3′-aryliminocoumarins) **6–20** as a colorless solids.

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