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REACTIONS OF 3-(4-ARYL-2-THIAZOLYL)- AND 3-(2-BENZOTHIAZOLYL)- 2-IMINOCOUMARINS WITH N-NUCLEOPHILES

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The reaction of 3-(4-aryl-2-thiazolyl)- and 3-(2-benzothiazolyl)-2-iminocoumarins with N-nucleophiles was studied. This reaction gives 2-N-substituted 3-(4-aryl-2-thiazolyl)- and 3-(2-benzothiazolyl)-iminocourmarins. N-Nucleophiles such as arylamines, heterocyclic amines, and hydrazine derivatives undergo this reaction.

Keywords: 3-(4-aryl-2-thiazolyl)-2-iminocoumarins, 3-(2-benzothiazolyl)-2-iminocoumarins, 2-iminocoumarins, nucleophilic substitution.

The synthesis, structure, and reactivity of 2-iminocoumarins have been studied intensively in the past decade [1-3]. Many of these compounds have found use as dyes for various purposes [4, 5] and have interesting biological activity [6]. On the other hand, N-substituted derivatives of 2-iminocoumarins have not been studied extensively [7-9].

Several approaches exist for the synthesis of N-substituted 2-iminocoumarins involving the reaction of 2-thiocoumarins [10], dialkylacetals of coumarins [11], and salts of 2-ethoxybenzopyrilium [8] or 2-iminocoumarins [7] with N-nucleophiles. The synthesis of N-substituted 2-iminocoumarins is most conveniently carried out with 2-iminocoumarins as the starting reagents. We should note that some N-substituted 2-iminocoumarin-3-carboxamides may appear as intermediates in the synthesis of various 3-hetarylcoumarins [12, 13].

In the present work, we studied the reactions of 3-(4-aryl-2-thiazolyl)- and 3-(2-benzothiazolyl)-2-iminocoumarins with various N-nucleophiles.

The starting 3-thiazolyl-2-iminocoumarins **3a-i, 4a,b** were obtained according to our previous procedure [3] by the condensation of aldehydes **1a-e** with the corresponding nitriles **2a-f** in 2-propanol in the presence of catalytic amounts of piperidine; these nitriles have an active methylene group. The reaction of these iminocoumarins with primary amines was carried out in ethanol, butanol, and DMF in the presence of catalytic amounts of sulfuric acid or acetic acid. The reaction of 3-thiazolyl-2-iminocoumarins **3a-i, 4a,b** with 1.5-2 equivalents of N-nucleophiles **5a-q** in DMF at reflux in the presence of catalytic amounts of sulfuric acid leads to the greatest yields of the final products. This procedure gave a series of N-substituted 3-[4-(4-R^2-phenyl)-2-thiazolyl]-2-iminocoumarins **6a-u:**

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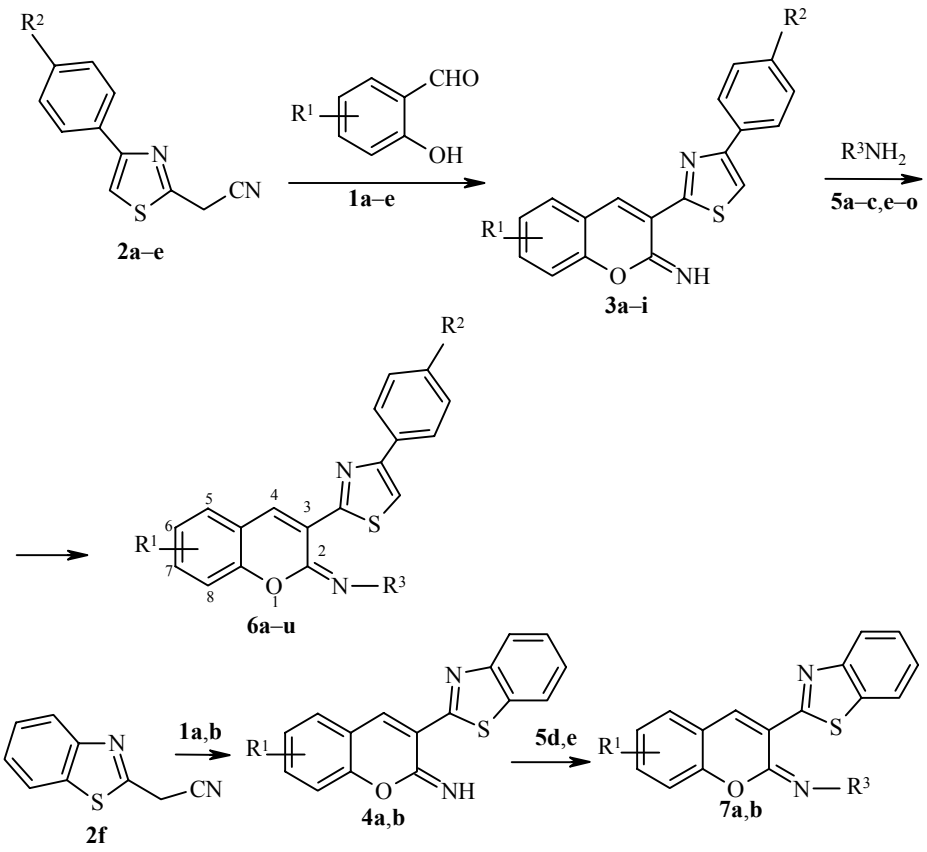

1 a R^1 = H, **b** R^1 = 4-NEt_2, **c** R^1 = 4-OH, **d** R^1 = 5-Cl, **e** R^1 = 5,6-benzo; **2 a** R^2 = H, **b** R^2 = Me, **c** R^2 = Cl, **d** R^2 = Br, **e** R^2 = NO_2;
3 a-c R^1 = H, **d-f** R^1 = 7-NEt_2, **g** R^1 = 7-OH, **h** R^1 = 6-Cl, **i** R^1 = 5,6-benzo, **a** R^2 = H, **b** R^2 = Me, **c** R^2 = NO_2, **d** R^2 = Me, **e** R^2 = Cl,
f, g R^2 = Br, **h** R^2 = Cl, **i** R^2 = Me; **4 a** R^1 = H, **b** R^1 = 7-NEt_2; **5 a** R^3 = Ph, **b** R^3 = *o*-MeC_6H_4, **c**, **e** R^3 = *p*-MeC_6H_4,
d R^3 = *o*-$MeOC_6H_4$, **f** R^3 = *m*-BrC_6H_4, **g** R^3 = *p*-$Me_2NC_6H_4$, **h** R^3 = *p*-$O_2NC_6H_4$, **i** R^3 = 2-thiazolyl, **j** R^3 = α-Py, **k** R^3 = NHPh,
l R^3 = NHCOPh, **m** R^3 = $NHCOCH_2CN$, **n** R^3 = $NHCOCH_2Py^+Cl^-$, **o** R^3 = $NHCSNH_2$, **p** R^3 = $NHCONH_2$, **q** R^3 = OH;
6 a-i R^1 = H, **j-r** R^1 = –NEt_2, **s** R^1 = 7-OH, **t** R^1 = 6-Cl, **u** R^1 = 5,6-benzo; **a-e** R^2 = H, **f-h** R^2 = Me, **i** R^2 = NO_2, **j**, **k** R^2 = Me,
l-n R^2 = Cl, **o-s** R^2 = Br, **t** R^2 = Cl, **u** R^2 = Me; **a**, **l**, **t** R^3 = Ph, **b**, **j** R^3 = *p*-$Me_2NC_6H_4$, **c** R^3 = *m*-BrC_6H_4, **d, q** R^3 = NHPh,
e R^3 = $NHCOCH_2Py^+Cl^-$, **f** R^3 = NHCOPh, **g** R^3 = $NHCOCH_2CN$, **h** R^3 = $NHCSNH_2$, **i** R^3 = *p*-$MeOC_6H_4$, **k** R^3 = *p*-$O_2NC_6H_4$,
m R^3 = 2-thiazolyl, **n** R^3 = $NHCONH_2$, **o** R^3 = *o*-MeC_6H_4, **p** R^3 = α-Py, **r**, **u** R^3 = OH, **s** R^3 = *p*-MeC_6H_4;
7 a R^1 = H, **b** R^1 = 7-NEt_2, **a** R^3 = *p*-$MeOC_6H_4$; **b** R^3 = *o*-$MeOC_6H_4$

Aromatic amines of varying basicity (from *p*-dimethylaminoaniline to *p*-nitroaniline) and heterocyclic amines such as α-aminopyridine and 2-aminothiazole readily undergo this reaction. No product was isolated in the case of sterically hindered *o*-bromoaniline. The presence of other *ortho* substituents in the nucleophile leads only to a slight drop in the yield of the product (Table 1). The products of condensation with such nucleophiles as phenylhydrazine, the hydrazides of benzoic and cyanoacetic acid, Girard reagent P (1-(carbazoylmethyl)-pyridinium chloride), thiosemicarbazide, semicarbazide, and hydroxylamine were obtained under similar conditions. The use of acid catalysis in butanol at reflux proved more suitable for the synthesis of N-substituted 3-benzothiazolyl-2-iminocoumarins **7a** and **7b**.

3-Thiazolyl-2-iminocoumarins **6a-u, 7a,b** are fine crystalline compounds ranging in color from light yellow to dark red. The solubility of these products in usual organic solvents such as ethanol, acetonitrile, and DMF ranges considerably depending on the nature of the substituents.

The electronic absorption spectra (EAS) of solutions of these products at 250-550 nm show two or more maxima (Table 1). In the case of 2-iminocoumarins without substituents in the coumarin part (R^1 = H) and lacking strong electron-donor or strong electron-withdrawing substituents, the electronic absorption spectra are

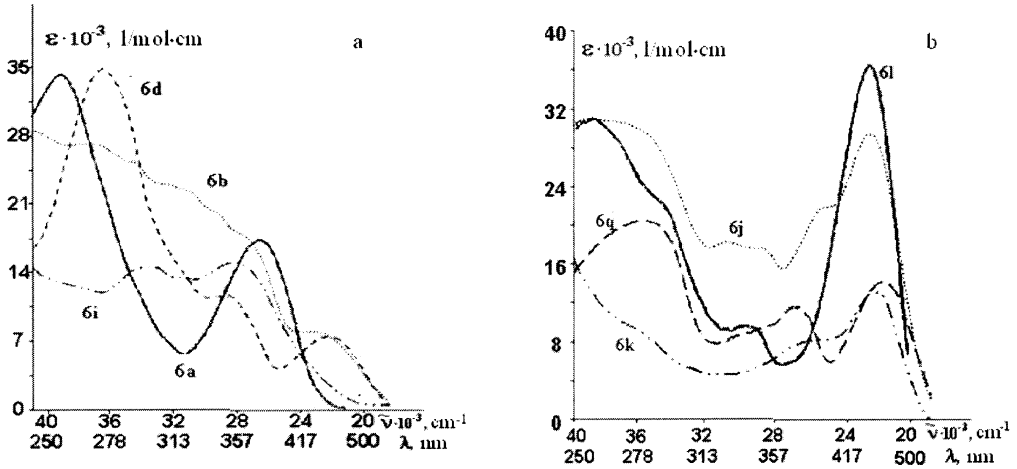

Fig. 1. Electronic absorption spectra of **6a,b,d,i** (*a*) and **6j,k,l,q** (*b*).

characteristic for 3-hetarylcoumarins and 3-hetaryl-2-iminocoumarins unsubstituted at the imino group such as **6a** ($R^1 = R^2 = H$, $R^3 = Ph$, Fig. 1a) and the long-wavelength maximum is found at virtually the same wavelength (376 nm) as in the spectrum of 3-(4-phenyl-2-thiazolyl)-2-iminocoumarin (375 nm) [15].

These findings suggest a small effect for substituent $R^3 = Ph$ on the absorption of the coumarin chromophore. On the other hand, the absorption spectrum is considerably altered upon the introduction of electron-donor substituents ($R^3 = p\text{-}Me_2NC_6H_4$ in **6b** and $R^3 = NHPh$ in **6d**). The strong bathochromic shift of the long-wavelength maximum (δ = 59 nm for **6b** and 72 nm for **6d**) indicates conjugation in the new chromophore system with significant participation of substituent R^3 in the imino group (Fig. 1a). The effect of substituent R^2 is pronounced only in the case of $R^2 = NO_2$ in **6i**. The hypsochromic shift of the long-wavelength absorption band (23 nm) and significant change in the overall shape of the spectrum in this case demonstrate the possible effect of substituent R^2 on the electronic structure of the chromophore system. The introduction of a strongly electron-donating N,N-dimethylamino group at $C_{(7)}$ in the coumarin system ($R^1 = NEt_2$) leads to a change in the electronic spectrum characteristic for 3-thiazolylcoumarins with an increase in intensity and a significant bathochromic shift of the long-wavelength band (72 nm, Fig. 1b for **6l**) in comparison with unsubstituted coumarins. Variation in the electronic nature of substituent R^3 significantly affects the shape of the spectrum ($R^3 = p\text{-}Me_2NC_6H_4$ in **6j**, $R^3 = NHPh$ in **6q**, and $R^3 = pO_2NC_6H_4$ in **6k**, Fig. 1b), while the position of the maximum of the long-wavelength band is not as strongly affected.

The IR spectra of all the compounds synthesized show a strong band for vibration of the C=N bond in the iminolactone group of the coumarin system at 1596-1708 cm^{-1}. Bands for the C=C bonds of the aromatic and heteroaromatic systems appear at 1502-1613 cm^{-1}. The bands at 1555-1708 cm^{-1} for **6e-g,n** correspond to vibrations of the C=O bonds in the hydrazide group. Weak bands for the vibrations of the C–H alkyl bonds of substituents R^2 and R^3 are found at 2785-2910 cm^{-1}. Medium-intensity bands characteristic for the diethylamino group are seen for the 7-N,N-diethylamino derivatives at 2962-2675 cm^{-1}. Weak bands for the vibrations of the aromatic and heteroaromatic C–H bonds appear at 3046-3117 cm^{-1}. The bands for the vibrations of the OH and NH groups appear at 3150-3462 cm^{-1}. The rather low frequencies of several NH groups in **6f** (3192 cm^{-1}) and **6h** (3150 cm^{-1}) suggest formation of strong hydrogen bonds in these compounds in the solid state (Table 1).

The ^1H NMR spectra given in Table 2 for **6g** and **6e** show signals for the minor isomeric form, which probably result from *E,Z*-isomerism of the C=N bond. While the singlet for the coumarin 8-H proton is at higher field than the doublet for the 6-H proton in all the spectra of the N,N-diethylamino derivatives, the reverse sequence is found for **6q** ($R^3 = NHPh$) and **6n** ($R^3 = NHCONH_2$), probably as a consequence of the formation of N–H···O intramolecular hydrogen bonds in these compounds.

TABLE 1. Characteristics of **6a-u, 7a,b**

Com-pound	Empirical formula	Found N % / Calculated N, %	mp, °C	IR spectrum, ν, cm^{-1}	UV spectrum (ethanol), λ, nm ($\varepsilon \cdot 10^{-3}$, l/mol·cm)*	Yield, %
1	2	3	4	5	6	7
6a	$C_{24}H_{16}N_2OS$	7.40 / 7.36	176-177	1557, 1588; 1646; 3087	255 (34.2); 376 (17.2)	65
6b	$C_{26}H_{21}N_3OS$	9.89 / 9.92	230-232	1553,1599; 1642; 2785; 3101	242 (28.7); 268 (27.3); 435 (7.8)	82
6c	$C_{24}H_{15}BrN_2OS$	6.06 / 6.10	172-173	1558, 1585,1600; 1653; 3048	256 (37.2); 376 (19.1)	59
6d	$C_{24}H_{17}N_3OS$	10.67 / 10.63	245-246	1509, 1580; 1596; 3098; 3378	274 (34.8); 351 (11.5); 448 (7.3)	87
6e	$C_{25}H_{19}ClN_4O_2S$	11.69 / 11.80	238-239	1600; 1638; 1691; 3065; 3430	385 (14.5)	83
6f	$C_{26}H_{19}N_3O_2S$	9.63 / 9.60	250-252	1511, 1594; 1638; 1655; 2925; 3100; 3192	264 (36.8); 382 (16.3)	78
6g	$C_{22}H_{16}N_4O_2S$	14.07 / 13.99	>300	1602; 1645; 1683; 2911, 2934; 3065, 3100; 3404	386 (16.2)	90
6h	$C_{20}H_{16}N_4OS_2$	14.32 / 14.27	248-250	1500, 1592; 1635; 2910; 3105; 3150, 3265, 3425	221 (26.0); 270 (34.0); 390 (14.2)	86
6i	$C_{25}H_{17}N_3O_4S$	9.19 / 9.23	264-266	1503, 1598; 1655; 2830; 2991, 3061	227 (19.1); 298 (14.5); 353 (15.0)	63
6j	$C_{31}H_{32}N_4OS$	10.95 / 11.01	195-197	1510, 1592, 1610; 1652; 2805, 2910, 2975; 3075, 3117	255 (30.9); 324 (18.3); 451 (29.2)	72
6k	$C_{29}H_{26}N_4O_3S$	11.08 / 10.97	250-251	1502, 1559, 1584; 1634; 2872, 2962; 3079	229 (30.7); 461 (13.5)	25
6l	$C_{28}H_{24}ClN_3OS$	8.62 / 8.65	248-249	1511, 1585, 1606; 1658; 2923, 2976; 3080	256 (30.9); 337 (9.5); 448 (36.2)	90
6m	$C_{25}H_{21}ClN_4OS_2$	11.39 / 11.36	234-235	1511, 1579; 1640; 2920, 2965; 3072, 3108	230 (23.5); 287 (19.9); 357 (21.6); 474 (34.1)	63

TABLE 1 (continued)

1	2	3	4	5	6	7
6n	$C_{23}H_{22}ClN_5O_2S$	14.93 14.97	265-266	1583, 1603; 1640; 1708; 2924, 2970; 3108; 3392, 3462	260 (32.6); 324 (6.6); 451 (31.5)	81
6o	$C_{29}H_{26}BrN_3OS$	7.83 7.72	192-193	1512, 1590, 1611; 1666; 2926, 2965	265 (27.3); 336 (5.4); 441 (36.8)	64
6p	$C_{27}H_{23}BrN_4OS$	10.45 10.54	227-228	1582, 1613; 1658; 2924, 2965; 3091	268 (29.2); 338 (8.7); 446 (40.0)	66
6q	$C_{28}H_{25}BrN_4OS$	10.25 10.27	243-244	1506, 1588, 1602; 1630; 2920, 2965; 3092; 3365	270 (31.4); 389 (11.1); 452 (26.1)	95
6r	$C_{22}H_{20}BrN_3O_2S$	8.87 8.93	268-269	1508, 1587, 1603; 1641; 2923, 2968; 3112; 3302	251 (31.8); 313 (7.7); 433 (34.0)	50
6s	$C_{25}H_{17}BrN_2O_2S$	5.78 5.72	245-247	1568, 1598; 1650; 2905; 3095; 3292	269 (37.2); 394 (20.1)	70
6t	$C_{24}H_{14}Cl_2N_2OS$	6.21 6.23	230-232	1562, 1591; 1643; 3090	385 (16.4)	68
6u	$C_{23}H_{16}N_2O_2S$	7.25 7.29	238-239	1512, 1565, 1582; 1685; 2911; 3059, 3102; 3426	252 (93.6); 411 (30.3)	72
7a	$C_{23}H_{16}N_2O_2S$	7.21 7.29	180-181	1563, 1590; 1651; 2834; 3046	266 (19.1); 291 (22.1); 325 (18.7); 398 (10.7)	81
7b	$C_{27}H_{25}N_3O_2S$	9.19 9.22	244-246	1515,1582,1610; 1668; 2821, 2921, 2966; 3055	295 (14.7); 453 (42.8)	59

* UV spectra of compounds **6c**,**f**,**l**,**q**,**s** and **7a** taken in MeCN solution, for compounds **6e**,**g**,**t** – in DMF solution.

TABLE 2. ^{1}H NMR Spectra of **6a-u, 7a,b**

Com-pound	Chemical shifts δ, ppm						
	4-H coumarin	5-H thiazole	CH coumarin	CH arom at thiazole $C_{(4)}$	CH arom. in R^3	CH aliphat.	NH, OH
1	2	3	4	5	6	7	8
6a	8.68	7.88	7.18 (1H, d, 8-H); 7.38-7.46 (2H, m, 6-, 7-H); 7.68 (1H, d, 5-H)	7.23 (1H, t, 4-H); 7.26-7.38 (4H, m, 2-, 3-, 5-, 6-H)	7.10 (1H, t, 4-H); 7.26-7.38 (4H, m, 2-, 3-, 5-, 6-H)	—	—
6b	8.63	8.23	7.23-7.61 (1H, d, 8-H); 7.23-7.61 (2H, m, 6-, 7-H); 7.81 (1H, d, 5-H)	7.23-7.61 (5H, m, 2-, 3-, 4-, 5-, 6-H)	6.80 (2H, d, 3-, 5-H); 8.11 (2H, d, 2-, 6-H)	2.94 (6H, s, CH_3Ar)	—
6c	8.80	8.10	6.55 (1H, d, 8-H); 7.15-7.58 (2H, m, 6-, 7-H); 7.80 (1H, d, 5-H)	7.15-7.58 (5H, m, 2-, 3-, 4-,5-,6-H)	8.08 (1H, s, 2-H); 7.15-7.58 (3H, m, 4-, 5-, 6-H);	—	—
6d	8.23	8.18	7.25 (1H, d, 8-H); 7.40-7.50 (2H, m, 6-, 7-H); 7.62 (1H, d, 5-H)	7.19 (1H, t, 4-H); 7.29-7.38 (4H, m, 2-, 3-, 5-, 6-H)	6.75 (1H, t, 4-H); 7.29-7.38 (4H, m, 2-, 6-, 5-, 3-H)	—	9.60 (1H, s, NH)
6e	8.63	8.24	7.20-7.45 (1H, m, 8-H); 7.48-7.70 (2H, m, 6-, 7-H); 7.8 (1H, d, 5-H)	7.20-7.45 (2H, m, 3-, 5-H); 8.02 (2H, d, 2-, 6-H); 7.62 (1H, s, 4-H)	8.25 (2H, m, 3-, 5-H); 8.45 (1H, t, 4-H); 9.22 (2H, d, 2-, 6-H)	6.20 (2H, s, CH_2)	11.90 (1H, s, NH)
6f	8.48	8.08	7.20-7.32 (1H, m, 8-H); 7.38-7.60 (2H, m, 6-, 7-H); 7.69 (1H, d, 5-H)	7.20-7.32 (2H, m, 3-, 5-H); 7.85-7.98 (2H, m, 2-, 6-H)	7.38-7.60 (3H, m, 4-, 3-, 5-H); 7.85-7.98 (2H, m, 2-, 6-H)	2.35 (3H, s, CH_3)	11.08 (1H, s, NH)
6g	8.49	8.23	7.33-7.61 (3H, m, 6-, 7-, 8-H) 7.77 (1H, d, 5-H)	7.32 (2H, d, 3-, 5-H); 7.98 (2H, d, 2-, 6-H)	—	2.38 (3H, s, CH_3); 4.30 (2H, s, CH_2)	11.35 (1H, s, NH)
6h	8.46	8.09	7.27 (1H, d, 8-H); 7.45-7.56 (2H, m, 6-, 7-H); 7.71 (1H, d, 5-H)	7.24 (2H, d, 3-, 5-H); 7.94 (2H, d, 2-, 6-H)	—	2.40 (3H, s, CH_3Ar)	7.05 (1H, s, NH); 8.48 (1H, s, NH); 10.30 (1H, br. s, NH) (diffuse)
6i	8.68	8.44	7.21-7.32 (2H, m, 6-, 8-H); 7.48 (1H, t, 7-H); 7.77 (1H, d, 5-H)	8.24 (2H, d, 2-, 6-H); 8.33 (2H, d, 3-, 5-H)	6.96 (2H, d, 3-, 5-H); 7.44 (2H, d, 2-, 6-H)	3.80 (3H, s, CH_3Ar);	—
6j	8.43	7.62	6.34 (1H, s, 8-H); 6.53 (1H, d, 6-H); 7.36 (1H, d, 5-H)	7.53 (2H, d, 3-, 5-H); 7.90 (2H, d, 2-, 6-H)	6.72 (2H, d, 3-, 5-H); 7.43 (2H, d, 2-, 6-H)	1.21 (6H, t, $\underline{CH_3}CH_2$); 2.41 (3H, s, CH_3Ar); 3.00 (6H, s, $2CH_3Ar$); 3.48 (4H, q, $\underline{CH_2}CH_3$)	—
6k	8.70	7.87	6.34 (1H, s, 8-H); 6.67 (1H, d, 6-H); 7.55 (1H, d, 5-H)	7.23 (2H, d, 3-, 5-H); 7.94 (2H, d, 2-, 6-H)	7.45 (2H, d, 2-, 6-H); 8.25 (2H, d, 3-, 5-H)	1.15 (6H, t, $\underline{CH_3}CH_2$); 2.35 (3H, s, CH_3Ar); 3.40 (4H, q, $\underline{CH_2}CH_3$)	—

TABLE 2 (continued)

1	2	3	4	5	6	7	8
6l	8.61	8.03	6.32 (1H, s, 8-H); 6.64 (1H, d, 6-H); 7.58 (1H, d, 5-H)	7.49 (2H, d, 3-, 5-H); 8.13 (2H, d, 2-, 6-H)	7.12 (1H, t, 4-H); 7.35 (2H, d, 2-, 6-H); 7.40 (2H, t, 3-, 5-H);	1.19 (6H, t, $\underline{CH_3}CH_2$); 3.45 (4H, q, $\underline{CH_2}CH_3$)	—
6m	8.78	8.06	6.67 (1H, s, 8-H); 6.84 (1H, d, 6-H); 7.73 (1H, d, 5-H)	7.48 (2H, d, 3-, 5-H); 7.67 (2H, d, 2-, 6-H)	7.40 (1H, d, 4-H); 8.14 (1H, d, 5-H)	1.22 (6H, t, $\underline{CH_3}CH_2$); 3.53 (4H, q, $\underline{CH_2}CH_3$)	—
6n	8.31	8.18	6.61 (1H, d, 6-H); 6.78 (1H, s, 8-H); 7.47 (1H, d, 5-H)	7.52 (2H, d, 3-, 5-H); 8.16 (2H, d, 2-, 6-H)	—	1.21 (6H, t, $\underline{CH_3}CH_2$); 3.45 (4H, q, $\underline{CH_2}CH_3$)	6.22 (2H, s, NH_2); 9.44 (1H, s, NH)
6o	8.59	7.97	6.18 (1H, s, 8-H); 6.60 (1H, d, 6-H); 7.49 (1H, d, 5-H)	7.59 (2H, d, 3-, 5-H); 8.03 (2H, d, 2-, 6-H)	6.95-7.28 (4H, m, 3-, 4-, 5-, 6-H)	1.19 (6H, t, $\underline{CH_3}CH_2$); 2.28 (3H, s, CH_3Ar); 3.41 (4H, q, $\underline{CH_2}CH_3$)	—
6p	8.72	8.41	6.22 (1H, s, 8-H); 6.64 (1H, d, 6-H); 7.49 (1H, d, 5-H)	7.58 (2H, d, 3-, 5-H); 7.98 (2H, d, 2-, 6-H)	7.15 (2H, m, 4-, 6-H); 7.72 (1H, t, 5-H); 7.81 (1H, s, 3-H)	1.22 (6H, t, $\underline{CH_3}CH_2$); 3.46 (4H, q, $\underline{CH_2}CH_3$)	—
6q	8.13	8.10	6.57 (1H, d, 6-H); 6.68 (1H, s, 8-H); 7.42 (1H, d, 5-H)	7.65 (2H, d, 3-, 5-H); 8.02 (2H, d, 2-, 6-H)	6.76 (1H, t, 4-H); 7.15-7.38 (4H, m, 2-, 6-, 5-, 3-H)	1.20 (6H, t, $\underline{CH_3}CH_2$); 4.45 (4H, q, $\underline{CH_2}CH_3$)	9.21 (1H, s, NH)
6r	8.17	8.12	6.44 (1H, s, 8-H); 6.55 (1H, d, 6-H); 7.42 (1H, d, 5-H)	7.64 (2H, d, 3-, 5-H); 8.01 (2H, d, 2-, 6-H)	—	1.13 (6H, t, $\underline{CH_3}CH_2$); 3.41 (4H, q, $\underline{CH_2}CH_3$)	10.48 (1H, s, OH)
6s	8.65	8.05	6.55 (1H, s, 8-H); 6.71 (1H, d, 6-H); 7.52 (1H, d, 5-H)	7.58 (2H, d, 3-, 5-H); 8.02 (2H, d, 2-, 6-H)	7.15 (2H, d, 3-, 5-H); 7.25 (2H, d, 2-, 6-H)	2.43 (3H, s, CH_3Ar)	10.4 (1H, s, OH)
6t	8.72	8.17	7.21 (1H, d, 8-H); 7.47 (1H, d, 7-H); 7.84 (1H, d, 5-H)	7.45 (2H, d, 3-, 5-H); 8.10 (2H, d, 2-, 6-H)	7.15 (1H, t, 4-H); 7.31-7.41 (4H, m, 2-, 6-, 3-, 5-H)	—	—
6u	8.91	8.09	7.47 (1H, d, 10-H); 7.64 (1H, d, 5-H); 7.74 (1H, t, 7-H); 7.87-8.15 (2H, m, 6-, 8-H); 8.45 (1H, d, 9-H)	7.30 (2H, d, 3-, 5-H); 7.87-8.15 (2H, m, 6-, 8-H)	—	—	10.63 (1H, s, OH)
7a	8.77	—	7.23-7.31 (1H, m, 8-H); 7.46-7.57 (2H, m, 6-, 7-H); 7.82 (1H, d, 5-H)	7.23-7.31 (1H, m, 5-H); 7.44 (1H, t, 6-H); 8.02 (1H, d, 7-H); 8.09 (1H, d, 4-H)	6.97 (2H, d, 3-, 5-H); 7.46-7.57 (2H, m, 2-, 6-H)	3.77 (3H, s, CH_3Ar)	—
7b	8.64	—	6.15 (1H, s, 8-H); 6.52 (1H, d, 6-H); 7.35-7.45 (1H, m, 5-H)	7.27 (1H, t, 5-H); 7.35-7.45 (1H, m , 6-H); 7.84-7.92 (2H, m, 7-, 4-H)	6.86-6.98 (2H, m, 5-, 4-H); 7.00-7.08 (2H, m, 2-, 6-H)	1.19 (6H, t, $\underline{CH_3}CH_2$); 3.40 (4H, q, $\underline{CH_2}CH_3$); 3.82 (3H, s, CH_3Ar)	—

Our study has shown that 2-imino-3-thiazolylcoumarins react with N-nucleophiles under acid catalysis conditions to give N-substituted 3-thiazolyl-2-iminocoumarins.

EXPERIMENTAL

The electronic absorption spectra were taken on a Hitachi U-3210 spectrophotometer. The IR spectra were taken for KBr pellets on a Specord IR-75 spectrometer at from 400 to 4000 cm^{-1}. The ^1H NMR spectra were taken on a Bruker 300 spectrometer at 300 MHz in DMSO-d_6 with TMS as the internal standard. The purity of all the compounds was checked by thin-layer chromatography on 200×200-mm Silufol plates using 1:2 ethyl acetate–toluene as the eluent.

The physicochemical and spectral indices of **6** and **7** are given in Tables 1 and 2.

N-Substituted 2-Imino-3-[4-(4-R^2-phenyl)-2-thiazolyl)]coumarins 6a-u (General Method). A sample of 2-iminocoumarin (3 mmol) was dissolved in DMF (10 ml) and amino compound (4.5-6.0 mmol) and 10% H_2SO_4 (3-5 drops) in methanol were added. The mixture was heated at reflux for 15-20 min. After cooling, the solution was diluted with a 10-fold volume of methanol. The precipitate was filtered off and recrystallized from a suitable solvent (toluene or acetonitrile).

N-Substituted 3-Benzothiazolyl-2-iminocoumarins 7a and 7b (General Method). A sample of 2-iminocoumarin (3 mmol) was dissolved in a minimal amount of hot butanol and substituted aniline (4.5-6 mmol) along with 2-3 drops 10% H_2SO_4 in methanol was added. The mixture was heated at reflux for 30-90 min. After cooling, the precipitate formed was filtered off and recrystallized from a suitable solvent (butanol or acetonitrile).

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