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3-Acyl-2-furylthiochromones: a new family of compounds with photoinduced fluorescence

Konstantin A. Chudov,*^a Konstantin S. Levchenko,^b Valery A. Barachevskii,^c Tat'yana M. Valova,^c Evgeny P. Grebennikov,^b Pavel S. Shmelin,^b Nikolai O. Poroshin,^b Grigory E. Adamov,^b Vladimir N. Yarovenko^a and Mikhail M. Krayushkin^a

^a N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian

Federation. Fax: +7 499 135 5328; e-mail: k4udov@gmail.com

^b Central Scientific and Research Technological Institute 'Technomash', 121108 Moscow, Russian Federation

^c Photochemistry Center, Russian Academy of Sciences, 119421 Moscow, Russian Federation

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New photosensitive 3-acyl-2-(2-furyl)thiochromones, potential components for multilayer media of archive-type optical discs, were prepared and tested for photorearrangement.



Compounds containing 3-(2-furyl)propenone system possess photoactive properties and are capable of photoinduced isomerization under UV irradiation giving fluorescent products. The derivatives of benzoquinones,¹ chromones,^{2,3} and tetralones^{4,5} are examples of such compounds. Recently, we obtained new representatives possessing photoinduced fluorescence such as derivatives of 2-aroyl-3-furylbenzofurans⁶ and 5-aroyl-4-furylthiazoles.⁷ Among the compounds synthesized previously, chromones are the best studied.^{2,3,8-10} Photoisomerization of these compounds is apparently of general character and can be exemplified by isomerization of 3-acyl-2-furylchromones **A**.^{2,3}



We have obtained a large series of 3-acyl-2-furylchromones with donor and acceptor substituents located at different positions of the molecule. The influence of their structures on the physical and chemical properties was revealed, and the possibility of their application as components of registering media in multilayer optical discs of extra high capacity with single-use, double-photon bit-by-bit (bitwise) record and fluorescent reading of optical information was proven.^{11–15}

This work is a continuation of a search for new photoactive compounds which can undergo irreversible photoisomerization giving fluorescent products. Here, we performed the synthesis and photochemical studies of 3-acyl-2-furylthiochromones, the closest analogues of 3-acyl-2-furylchromones.

To synthesize compounds **1a–c**, the methods similar to those used previously in a syntheses of 3-acyl-2-furylchromones¹² (Scheme 1) were employed. Thioacetophenone esters **2a,b** were obtained by acylation of 2-mercaptoacetophenone¹⁶ with benzoyl or 2-thenoyl chlorides in the presence of triethylamine. However, it appears that the classical conditions of the Baker–Venkataraman rearrangement (Bu^tOK in DMF) when applied to **2a,b** led to an



2, 3: a X = S, Ar = Ph b X = S, Ar = 2-thienyl c X = O, Ar = 2-thienyl d X = O, Ar = 2-thienyl h X = S, Ar = Ph, R = H b X = S, Ar = Ph, R = H c X = O, Ar = 2-thienyl d X = O, Ar = 2-thienyl d X = O, Ar = 2-thienyl h X = S, Ar = Ph, R = H h X = S, Ar = Ph, R = H h X = S, Ar = Ph, R = H h X = S, Ar = Ph, R = H h X = S, Ar = Ph, R = H h X = S, Ar = Ph, R = H h X = S, Ar = Ph, R = H h X = S, Ar = 2-thienyl h X = S, Ar = 2-thieny

Scheme 1 Reagents and conditions: i, X = S, ArC(O)Cl, CH_2Cl_2 , Et_3N or X = O, ArC(O)Cl, Py; ii, X = S, LDA (2 equiv.), THF, $-15-0^{\circ}C$ (Ar = Ph) or -78 to $-40^{\circ}C$ (Ar = 2-thienyl) or X = O, Bu^tOK, DMF, $-10-0^{\circ}C$; iii, 2-furaldehyde, piperidine (cat.), EtOH, $20-40^{\circ}C$; iv, SeO₂, dioxane, reflux.

inseparable mixture of products instead of diketones **3a,b**. Also, an attempted treatment of **2a** with lithium diisopropylamide (LDA) in THF¹⁷ followed by acidification afforded the cyclization product, 2-phenyl-4*H*-thiochromen-4-one. To avoid the cyclization, the reaction mixture was treated under neutral conditions providing the product **3a** in 63% yield.

To obtain diketone **3b** (27%), compound **2b** was treated with 2 equiv. of LDA at -70 to -40 °C in THF. Diketones **3a,b** were reacted with 2-furaldehyde and 5-methyl-2-furaldehyde giving the products existing in two forms: **4a–c** or **4'a–c**. Thiochromanones bearing benzoyl groups were isolated presumably as an enol form **4'**, which was confirmed by ¹H NMR spectra. The product of condensation of diketone **3b** with furaldehyde was isolated as a mixture of two forms (**4c**, **4'c**) and used for the next step without isolation of individual components. Compounds **4a–c** (**4'a–c**) were oxidized with 1.5 equiv. of SeO₂ in dioxane under reflux affording **1a–c** in 78–92% yields (see Scheme 1).[†]

Further oxidation of thiochromones **1a**,**b** with *m*-CPBA allowed us to obtain 1,1-dioxidothiochromones **5a**,**b** (Scheme 2).

The structures of **1a–c** and **5a,b** were confirmed by ¹H and ¹³C NMR, high-resolution mass spectra (HRMS); for compounds **1c** and **5a**, X-ray analysis was performed (Figures 1 and 2).[‡]

It is evident from Table 1 that the replacement of the oxygen atom (compound 1d) by sulfur in the chromone fragment (com-



Scheme 2 Reagents and conditions: i, m-CPBA, CH₂Cl₂.

[†] *Thiochromones* **1a–c** (general procedure). A mixrure of two forms **4a–c**/**4'a–c** (1 mmol) was dissolved in dioxane (2 ml), SeO₂ (1.5 mmol) was added, and the mixture was refluxed until the starting material disappeared (TLC control). Dioxane was removed under reduced pressure, the residue was dissolved in chloroform (5 ml) and the solution was filtered through a small column with silica gel with elution by a mixture of methylene chloride–light petroleum (1:1). After evaporation of the eluent, the resulting yellow crystals were washed with ethanol.

3-Benzoyl-2-(2-furyl)thiochromone **1a**. Yield 0.3 g (90%), mp 235–237 °C. ¹H NMR (300 MHz, CDCl₃) δ : 8.48 (d, 1H, *J* 8.0 Hz), 7.97 (d, 2H, *J* 7.4 Hz), 7.68 (d, 2H, *J* 3.7 Hz), 7.62–7.51 (m, 2H), 7.50–7.39 (m, 3H), 6.86 (d, 1H, *J* 3.6 Hz), 6.45 (dd, 1H, *J* 3.6, 1.7 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 195.46, 179.16, 146.87, 145.74, 138.36, 136.54, 136.20, 133.59, 132.11, 130.78, 130.42, 129.05, 128.84, 128.75, 127.97, 126.20, 114.90, 112.77. HRMS, *m*/*z*: 333.0585 [M + H]⁺, 355.0401 [M + Na]⁺, 371.0139 [M + K]⁺ (calc. for C₂₀H₁₂O₃S, *m*/*z*: 333.0580, 355.0399, 371.0139).

3-Benzoyl-2-(5-methylfuran-2-yl)thiochromone **1b**. Yield 0.32 g (92%), mp 192–194 °C. ¹H NMR (300 MHz, CDCl₃) δ : 8.46 (d, 1H, J 8.0 Hz), 7.97 (d, 2H, J 7.3 Hz), 7.64 (d, 2H, J 3.9 Hz), 7.59–7.49 (m, 2H), 7.43 (t, 2H, J 7.5 Hz), 6.75 (d, 1H, J 3.5 Hz), 6.04 (d, 1H, J 3.3 Hz), 2.17 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃) δ : 195.76, 179.17, 156.78, 145.10, 138.36, 136.70, 136.15, 133.44, 132.00, 130.41, 129.42, 129.03, 128.72, 128.68, 127.80, 126.15, 116.40, 109.46, 13.55. HRMS, m/z: 347.0737 [M + H]⁺, 369.0557 [M + Na]⁺, 385.0295 [M + K]⁺ (calc. for C₂₁H₁₄O₃S, m/z: 347.0736, 369.0556, 385.0295).

2-(2-Furyl)-3-(thiophen-2-ylcarbonyl)thiochromone **1c**. Yield 78%, mp 227–229 °C. ¹H NMR (300 MHz, CDCl₃) δ : 8.50 (d, 1H, *J* 8.0 Hz), 7.74–7.50 (m, 6H), 7.05 (t, 1H, *J* 4.3 Hz), 6.92 (d, 1H, *J* 3.6 Hz), 6.47 (dd, 1H, *J* 3.3, 1.5 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 187.31, 178.77, 146.69, 145.87, 143.87, 138.91, 136.07, 134.74, 134.02, 132.17, 130.47, 130.42, 128.89, 128.25, 128.04, 126.24, 115.16, 112.90. HRMS, *m/z*: 339.0144 [M + H]⁺, 360.9964 [M + Na]⁺, 376.9703 [M + K]⁺ (calc. for C₁₈H₁₀O₃S₂, *m/z*: 339.0147, 360.9959, 376.9703).

For more detail, see Online Supplementary Materials.



Figure 1 X-ray structure of 1c. The atoms are represented as thermal ellipsoids at 50% probability level.



Figure 2 X-ray structure of 5a. The atoms are represented as thermal ellipsoids at 50% probability level.

pound **1c**) results in appearance of two new long-wave absorption bands at 330 and 357 nm (sh) (Figure 3) thus making possible photoactivation of the latter compound with near UV light. Absorption band maximum for the photoproduct of compound **1c** has a batochromic shift of 10 nm, and the maximum of the fluorescence band has a hypsochromic shift of 17 nm as compared to the maxima of the corresponding bands for compound **1d**. Simultaneously, both compounds **1c** and **1d** have a comparable photosensitivity of formation of the photoproduct, which is determined as a photoinduced optical density at the maximum of the band of the photoproduct before the beginning of photodegradation normalized on the optical density in the absorption band maximum of the starting compound in the range of photoactivation $(D_{\text{max}}^{\text{max}}/D_{\text{max}}^{\text{max}})$ (Table 1). Compound **1c** has slightly smaller

[‡] Crystallographic data.

Intensities of 17241 and 19644 reflections for **1c** and **5a**, respectively, were measured with a Bruker APEX2 CCD diffractometer [λ (MoK α) = = 0.71072 Å, ω -scans, $2\theta < 58^{\circ}$], 3890 and 4330 independent reflections [$R_{int} = 0.0377$ and 0.0487] were used in further refinement for **1c** and **5a**, respectively. Structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. For **1c**, the refinement converged to $wR_2 = 0.0975$ and GOF = 1.047 for all independent reflections [$R_1 = 0.0369$ was calculated against *F* for 3134 observed reflections with $I > 2\sigma(I)$]. For **5a**, the refinement converged to $wR_2 = 0.0937$ and GOF = 1.003 for all independent reflections [$R_1 = 0.0405$ was calculated against *F* for 3819 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.¹⁸

CCDC 1443807 and 1443808 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Crystals of **1c** (C₁₈H₁₀O₃S₂, M = 338.38) are monoclinic, space group $P2_1/n$, at 120 K: a = 7.4352(6), b = 10.2324(7) and c = 19.3193(14) Å, $\beta = 95.189(2)^\circ$, V = 1463.79(19) Å³, Z = 4 (Z' = 1), $d_{calc} = 1.535$ g cm⁻³, μ (MoKα) = 3.76 cm⁻¹, F(000) = 696.

Crystals of **5a** ($C_{20}H_{12}O_5S$, M = 364.36) are orthorhombic, space group $P2_12_12_1$, at 120 K: a = 8.0407(6), b = 11.5563(9) and c = 17.5501(13) Å, V = 1630.8(2) Å³, Z = 4 (Z' = 1), $d_{calc} = 1.484$ g cm⁻³, μ (MoK α) = 2.29 cm⁻¹, F(000) = 752.

Table 1 Spectral kinetic characteristics of compounds 1 and 5.^a

Com- pound	$\lambda_{\rm max}^{\rm A}/$ nm	ϵ/dm^3 mol ⁻¹ cm ⁻¹	$\lambda_{ m max}^{ m B}/$ nm	$D_{ m max}^{ m B}/ D_{ m max}^{ m A}$	$\lambda_{\rm fl,max}^{\rm B}/$ nm	$\Delta\lambda/$ nm	I ^B _{fl,max} (arbitrary units)	$ au_{1/2}/s$
1a	293	15250	424	0.14	486	62	248	1580
	330	15750						
	357 (sh)							
1b	294	17500	422	0.10	494	72	372	457
	343	30000						
1c	294	18750	445	0.17	503	58	345	1545
	330	14750						
	357(sh)	11250						
1d	305	25000	435	0.15	520	85	464	897
5a	379	16750	362	0.29	488	126	9	630
5b	400	21500	342	0.35	482	140	12	127

 ${}^{a}\lambda^{A}_{max},\lambda^{B}_{max}$, and $\lambda^{B}_{l,max}$ are the wavelengths at maxima of absorption bands of forms **A** and **B** and a wavelength at maximum of fluorescence of form **B**, respectively; D^{A}_{max} and D^{B}_{max} are the optical densities at maxima of absorption bands of forms **A** and **B** before photodegradation of the compounds; $\Delta\lambda$ is the Stokes shift; $I^{B}_{l,max}$ is the fluorescence intensity in the maximum of fluorescence band in photoinduced form **B** before photodegradation; $\tau_{1/2}$ is the time during which the value of optical density in the maximum of the absorption band of form **B** is reduced twice under non-filtered irradiation with xenon lamp.



Figure 3 (1, 2) Absorption spectra, (3) fluorescence excitation measured at 503 nm and (4) fluorescence by excitation at 424 nm of chromone 1c in toluene (1) before and (2–4) after UV irradiation.

maximum of fluorescence intensity than that of chromone **1d**, however the stability of its photoproduct towards unfiltered irradiation is higher almost twice, which is important for practical use.

In a transfer from compound **1c** possessing thienol fragment to **1a** bearing benzoyl fragment, hypsochromic shifts of absorption bands (21 nm) and fluorescence (16 nm) of the photoproduct were observed along with the decrease in fluorescence intensity. Introduction of methyl substituent in furyl fragment (compound **1b**) results in strong increase in efficiency of photodegradation of the photoproduct and decrease in photosensitivity of the starting compound.

It is important to note that 1,1-dioxidothiochromones **5a,b**, in which sulfonyl fragments possess strong electron-acceptor effect, do not form photoproducts with long-wave absorption band under UV irradiation.

Figure 4 demonstrates the disappearance of the absorption band of compound **5b** in toluene with the maximum at 400 nm and simultaneous appearance of the photoproduct absorption band (the maximum at 342 nm). Similar behavior is observed for compound **5a**. Both compounds **5a**,**b** have weak fluorescence during excitation at the maximum of absorption of the photoproducts, but not at the absorption band maximum of the starting compound, which sufficiently increases the Stokes shift. Both compounds **5a**,**b** are less photochemically stable than their analogues **1a**,**b**.

A comparative analysis of properties of photoproducts (form **B**) of chromone **1d** and thiochromone **1c** was carried out. In ¹H NMR spectra of photoproducts, one can find two characteristic signals: signals of aldehyde protons at 9.67 and 9.70 ppm (d, *J* 7.9 Hz), respectively; signal of protons located at α -position to the aldehyde



Figure 4 Absorption spectra of compound **5b** in toluene (*1*) before and (2–8) after successive UV irradiation through UFS-1 light filter.

group, 6.65–6.75 ppm (dd, J 15.6, 7.9 Hz) for both photoproducts. In the EI mass spectrum (70 eV), the peaks of a molecular ion and a fragment of forms **B** [M–CHCHCHO]⁺ were detected.

In conclusion, we have synthesized new photosensitive 3-acyl-2-(2-furyl)thiochromones which undergo irreversible photoinduced transformations into fluorescent products. These compounds and their analogues could be considered as specific organic hybrid systems and serve as starting materials for the further synthesis of condensed products and components of optical memory.¹⁹

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.11.021.

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