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Synthesis of 2-Alkyl-1-aryl-1,2-dihydrochromeno[2,3-*c*]pyrrole-3,9-dione Derivatives

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Abstract—A preparative procedure for the synthesis of 2-alkyl-1-aryl-1,2-dihydrochromeno[2,3-*c*]pyrrole-3,9-diones from methyl 4-(o-hydroxyphenyl)-2,4-dioxobutanoate, aromatic aldehyde, and aliphatic amine is described.

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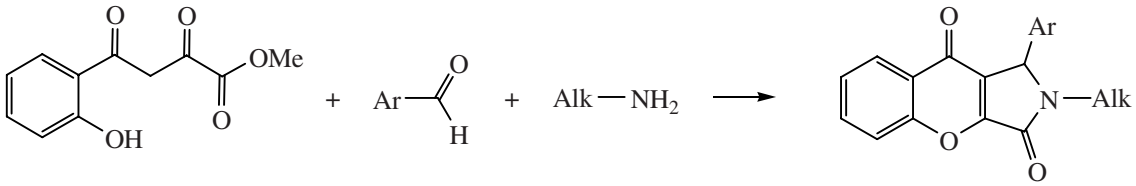
We previously [1, 2] found that methyl 4-(*o*-hydroxyphenyl)-2,4-dioxobutanoate is readily converted into 1,2-diaryl- or 1-aryl-2-hetaryl-1,2-dihydrochromeno[2,3-*c*]pyrrole-3,9-diones. In the present article we describe a convenient synthetic approach to hitherto unknown 2-alkyl-1-aryl-1,2-dihydrochromeno [2,3-*c*]pyrrole-3,9-diones starting from methyl 4-(*o*-hydroxyphenyl)-2,4-dioxobutanoate [3], aromatic aldehyde **IIa–IIg**, and aliphatic amine **III–VIII**, as shown in Scheme 1. By heating equimolar amounts of ester **I**, benzaldehyde, and methylamine in anhydrous ethanol we obtained 20% of 2-methyl-1-phenyl-1,2-dihydrochromeno[2,3-*c*]pyrrole-3,9-dione (**IXa**). Replacement of the solvent by methanol or propan-2-ol resulted in lower yields of the final product (≤15%), and the yield of **IXa** did not increase on prolonged heating (Table 1).

Obviously, the described transformation is a multistep process. In the first step, condensation of aromatic aldehyde with amine gives Schiff base **XV** which reacts with methyl 4-(*o*-hydroxyphenyl)-2,4-dioxobutanoate (Scheme 2). Intermediate **XVI** thus formed is converted into 1-alkyl-5-aryl-4-(2-hydroxybenzoyl)-3-hydroxy-2,5-dihydro-1*H*-pyrrol-2-one **XX** [4, 5], and dehydration of the latter yields chromone derivatives **IX–XIV**. An alternative mechanism is also possible. Intermediate adduct **XVI** is converted into substituted chromone **XVII** by the action of ester **I** (which is a weak acid), and compound **XVII** should readily undergo intramolecular ring closure to chromenopyrrole **IX–XIV** on heating [3]. Taking into account that prolonged reaction time does not affect the yield of the final product, the transformation **I** → **XVI** → **XX** → **IX–XIV** seems to be more probable.

Scheme 1.

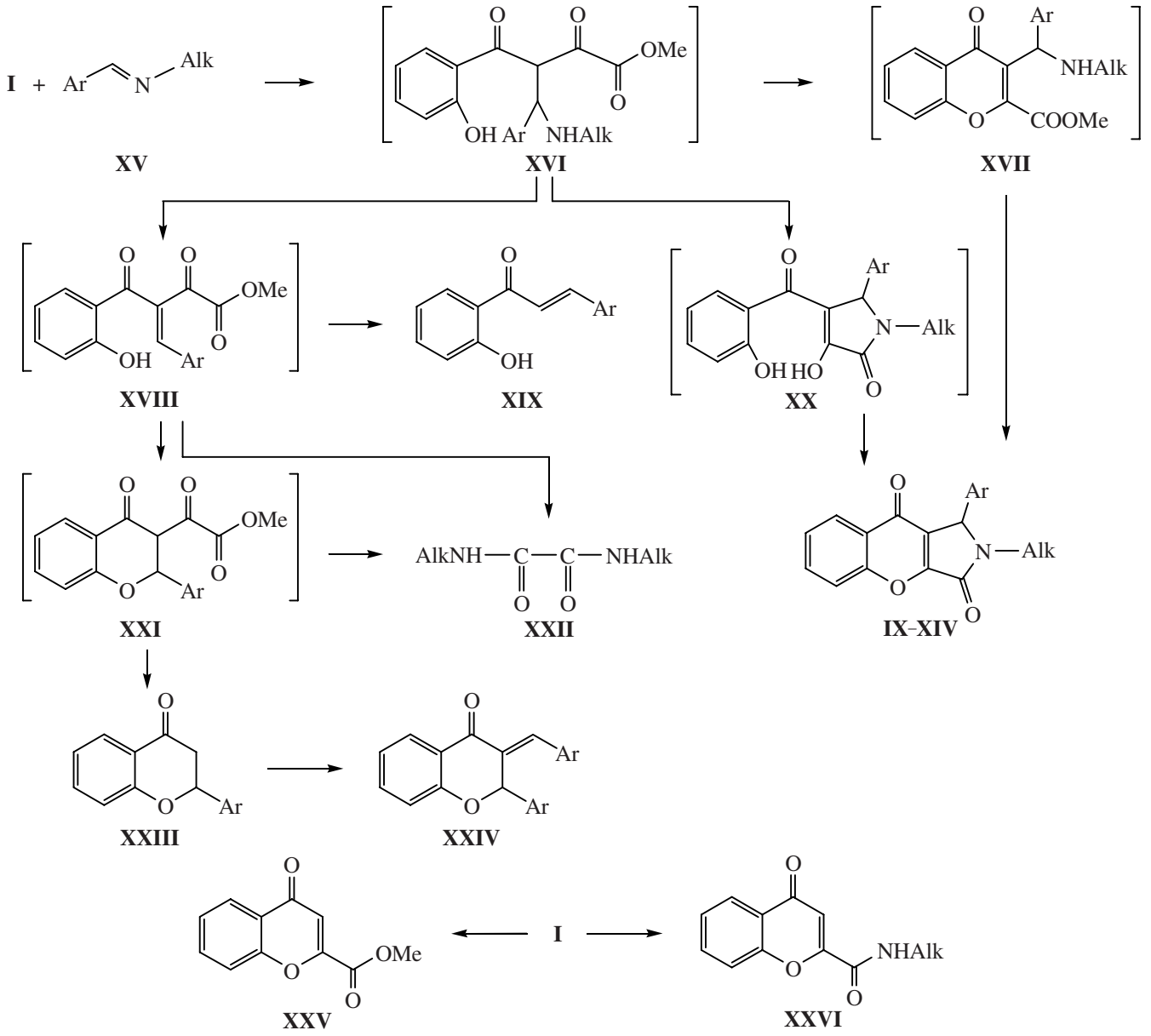


I **IIa–IIg** **III–VIII** **IXa–IXg; Xa, Xb, Xf; XIa, XIc, XIf; XIIa–XIId; XIIIa, XIIIb, XIIIf; XIVa, XIVb, XIVd**

Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-FC_6H_4 (**c**), 4-ClC_6H_4 (**d**), 4-$O_2NC_6H_4$ (**e**), 4-$MeOC_6H_4$ (**f**), 3,4-$(MeO)_2C_6H_3$ (**g**); **III**, **IXa–IXg**, Alk = Me; **IV**, **Xa**, **Xb**, **Xf**, Alk = Et; **V**, **XIa**, **XIc**, **XIf**, Alk = $MeOCH_2CH_2$; **VI**, **XIIa–XIId**, Alk = $PhCH_2$; **VII**, **XIIIa**, **XIIIb**, **XIIIf**, Alk = $PhCH_2CH_2$; **VIII**, **XIVa**, **XIVb**, **XIVd**, Alk = furfuryl.

The first steps of the process occur in basic medium, while dehydration of **XX** is more effective in acidic medium or in the presence of dehydrating agents. Therefore, we tried another procedure for the synthesis of chromone derivatives **IX–XIV**. Initially, a mixture of aromatic aldehyde and aliphatic amine was heated in anhydrous ethanol, methyl 4-(*o*-hydroxyphenyl)-2,4-dioxobutanoate was then added, the mixture was left to stand for 30 min and heated to the boiling point, acetic acid was added, and the mixture was heated further. As a result, we succeeded in isolating 2-alkyl-1-aryl-1,2-dihydrochromeno[2,3-*c*] pyrrole-3,9-diones **IX–XIV** in satisfactory yields. Obviously, the reaction is accompanied by other processes which considerably affect the yield of compounds **IX–XIV**. From the reaction mixtures we isolated compounds **XIX** and **XXII–XXVI** as individual substances. Presumably, adducts **XVI** exist in equilibrium with arylmethylidene derivatives **XVIII** which give rise to products **XIX** and **XXII–XXIV** (transformations **XVIII** → **XIX**, **XVIII** → **XXII**, **XVIII** → **XXI** → **XXII**, and **XVIII** → **XXI** →

Scheme 2.



For Ar, Alk see Scheme 1.

Table 1. Yields of 2-alkyl-1-phenyl-1,2-dihydrochromeno [2,3-*c*]pyrrole-3,9-diones **IXa**, **XIIa**, and **XIVa** in the three-component condensation of methyl 4-(*o*-hydroxyphenyl)-2,4-dioxobutanoate with benzaldehyde and amines

Comp. no.	Method	Solvent	Reaction time, h	Yield, %
IXa	*a*	Ethanol[a]	1	20
IXa	*a*	Ethanol[a]	4	18
IXa	*a*	Ethanol	1.5	12
IXa	*a*	Methanol	1.5	14
IXa	*a*	Propan-2-ol	1	8
IXa	*b*	–	–	55
XIIa	*a*	Ethanol[a]	0.5	10
XIIa	*b*	–	–	47
XIVa	*a*	Ethanol[a]	1.5	16
XIVa	*b*	–	–	61

[a] Anhydrous.

XXIII). Arylmethylidene-substituted chromones **XXIV** are formed by reaction of flavones **XXIII** with aldehydes or Schiff bases **XV**. Ester **I** is also converted into methyl 4-oxo-4*H*-chromene-2-carboxylate (**XXV**) and amides **XXVI**.

Compounds **XIX** and **XXII–XXVI** are formed in small amounts, so that chromones **IX–XIV** can be purified by crystallization. Exceptions are oxamides **XXII** that are formed as a result of two concurrent processes, and their mole fraction is always larger than those of other impurities. Nevertheless, their formation did not complicate purification of chromenopyrroles **IX–XI**, for the corresponding oxamides were readily soluble in the reaction mixture. The isolation of chromone derivatives **XII–XIV** was more difficult since concomitant oxamides **XXII** crystallized together with compounds **XII–XIV** from almost all solvents. The amount of oxamides **XXII** can be reduced by carrying out the reaction under argon; in this case, compounds **XII–XIV** can be isolated by

Table 2. IR and ^{1}H NMR spectra of 2-alkyl-1-aryl-1,2-dihydrochromeno[2,3-*c*]pyrrole-3,9-diones **IX**–**XIV**

Comp. no.	IR spectrum (KBr),[a] ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm
IXa	1610 (C=C); 1653 (C^9=O); 1708 (C^3=O)	2.83 s (3H, NCH_3), 5.61 s (1H, 1-H), 7.30–7.39 m (5H, H_{arom}) 7.52 m (1H, 7-H), 7.80–7.90 m (2H, 5-H, 6-H), 8.03 d.d (1H, 8-H)
IXb	1610 (C=C); 1655 (C^9=O); 1711 (C^3=O)	2.32 s (3H, CH_3), 2.82 s (3H, NCH_3), 5.55 s (1H, 1-H), 7.15–7.21 m (4H, 4H, H_{arom}), 7.52 m (1H, 7-H), 7.82–7.90 m (2H, 5-H, 6-H), 8.04 d.d (1H, 8-H)
IXc	1609 (C=C); 1655 (C^9=O); 1714 (C^3=O)	2.83 s (3H, NCH_3), 5.64 s (1H, 1-H), 7.11–7.19 m (2H, H_{arom}), 7.36–7.41 m (2H, H_{arom}) 7.52 m (1H, 7-H), 7.69–7.90 m (2H, 5-H, 6-H), 8.04 d.d (1H, 8-H)
IXd	1609 (C=C); 1657 (C^9=O); 1712 (C^3=O)	2.84 s (3H, NCH_3), 5.64 s (1H, 1-H), 7.36–7.41 m (4H, H_{arom}), 7.53 m (1H, 7-H), 7.79–7.90 m (2H, 5-H, 6-H), 8.03 d.d (1H, 8-H)
IXe	1612 (C=C); 1663 (C^9=O); 1724 (C^3=O)	2.88 s (3H, NCH_3), 5.83 s (1H, 1-H), 7.53 m (1H, 7-H), 7.69 d (2H, H_{arom}), 7.80–7.90 m (2H, 5-H, 6-H), 8.05 d.d (1H, 8-H), 8.22 d (2H, H_{arom})
IXf	1610 (C=C); 1656 (C^9=O); 1712 (C^3=O)	2.82 s (3H, NCH_3), 3.76 s (3H, OCH_3), 5.54 s (1H, 1-H), 6.89 d (2H, H_{arom}), 7.23 d (2H, H_{arom}) 7.52 m (1H, 7-H), 7.69–7.90 m (2H, 5-H, 6-H), 8.03 d.d (1H, 8-H)
IXg	1609 (C=C); 1656 (C^9=O); 1715 (C^3=O)	2.83 s (3H, NCH_3), 3.73 s (3H, OCH_3), 3.76 s (3H, OCH_3), 5.54 s (1H, 1-H), 6.83–6.91 m (3H, H_{arom}), 7.52 m (1H, 7-H), 7.69–7.90 m (2H, 5-H, 6-H), 8.03 d.d (1H, 8-H)
Xa	1609 (C=C); 1651 (C^9=O); 1702 (C^3=O)	1.06 t (3H, $^3J_{HH}$ 7.2 Hz, CH_3), 2.88 d. t (1H, $^2J_{HH}$ 14.2, $^3J_{HH}$ 7.2 Hz, $H_B NCH_2$), 3.69 d. t (1H, $^2J_{HH}$ 14.2, $^3J_{HH}$ 7.2 Hz, $H_A NCH_2$), 5.51 s (1H, 1-H), 7.30–7.39 m (5H, H_{arom}) 7.52 m (1H, 7-H), 7.80–7.90 m (2H, 5-H, 6-H), 8.03 d.d (1H, 8-H)
Xe	1610 (C=C); 1659 (C^9=O); 1711 (C^3=O)	1.08 t (3H, $^3J_{HH}$ 7.2 Hz, CH_3), 2.85 d. t (1H, $^2J_{HH}$ 14.4, $^3J_{HH}$ 7.2 Hz, $H_B NCH_2$), 3.72 d. t (1H, $^2J_{HH}$ 14.4, $^3J_{HH}$ 7.2 Hz, $H_A NCH_2$), 5.82 s (1H, 1-H), 7.53 m (1H, 7-H), 7.69 d (2H, H_{arom}), 7.80–7.90 m (2H, 5-H, 6-H), 8.05 d.d (1H, 8-H), 8.22 d (2H, H_{arom})
Xf	1609 (C=C); 1655 (C^9=O); 1708 (C^3=O)	1.06 t (3H, $^3J_{HH}$ 7.2 Hz, CH_3), 2.91 d. t (1H, $^2J_{HH}$ 14.4, $^3J_{HH}$ 7.2 Hz, $H_B NCH_2$), 3.68 d. t (1H, $^2J_{HH}$ 14.4, $^3J_{HH}$ 7.2 Hz, $H_A NCH_2$), 3.76 s (3H, OCH_3),5.63 s (1H, 1-H), 6.89 d (2H, H_{arom}), 7.23 d (2H, H_{arom}) 7.51 m (1H, 7-H), 7.69–7.90 m (2H, 5-H, 6-H), 8.03 d.d (1H, 8-H)
XIa	1610 (C=C); 1653 (C^9=O); 1713 (C^3=O)	2.89 m (1H, $H_B NCH_2$), 3.24 s (3H, OCH_3), 3.44 m (2H, OCH_2), 3.91 m (1H, $H_A NCH_2$), 5.72 s (1H, 1-H), 7.30–7.39 m (5H, H_{arom}) 7.52 m (1H, 7-H), 7.80–7.90 m (2H, 5-H, 6-H), 8.03 d.d (1H, 8-H)

Table 2. (Contd.)

Comp. no.	IR spectrum (KBr),[a] ν, cm^{-1}	^1H NMR spectrum, δ, ppm
XIc	1608 (C=C); 1652 (C^9=O); 1710 (C^3=O)	2.90 m (1H, H_B NCH_2), 3.24 s (3H, OCH_3), 3.45 m (2H, OCH_2), 3.86 m (1H, H_A NCH_2), 5.74 s (1H, 1-H), 7.11–7.18 m (2H, H_{arom}), 7.36–7.41 m (2H, H_{arom}) 7.53 m (1H, 7-H), 7.69–7.90 m (2H, 5-H, 6-H), 8.02 d.d (1H, 8-H)
XIf	1607 (C=C); 1652 (C^9=O); 1710 (C^3=O)	2.87 m (1H, H_B NCH_2), 3.24 s (3H, OCH_3), 3.44 m (2H, OCH_2), 3.76 s (3H, OCH_3), 3.86 m (1H, H_A NCH_2), 5.65 s (1H, 1-H), 6.89 d (2H, H_{arom}), 7.21 d (2H, H_{arom}) 7.52 m (1H, 7-H), 7.69–7.90 m (2H, 5-H, 6-H), 8.02 d.d (1H, 8-H)
XIIa	1609 (C=C); 1657 (C^9=O); 1713 (C^3=O)	3.84 d (1H, $^2J_{HH}$ 15.3 Hz, H_B NCH_2), 4.97 d (1H, $^2J_{HH}$ 15.3 Hz, H_A NCH_2), 5.39 s (1H, 1-H), 7.13–7.39 m (10H, H_{arom}) 7.51 m (1H, 7-H), 7.79–7.90 m (2H, 5-H, 6-H), 8.01 d.d (1H, 8-H)
XIIb	1608 (C=C); 1653 (C^9=O); 1714 (C^3=O)	2.33 s (3H, CH_3), 3.79 d (1H, $^2J_{HH}$ 15.3 Hz, H_B NCH_2), 4.97 d (1H, $^2J_{HH}$ 15.3 Hz, H_A NCH_2), 5.33 s (1H, 1-H), 7.11–7.35 m (9H, H_{arom}), 7.52 m (1H, 7-H), 7.80–7.90 m (2H, 5-H, 6-H), 8.01 d.d (1H, 8-H)
XIIc	1608 (C=C); 1654 (C^9=O); 1714 (C^3=O)	3.79 d (1H, $^2J_{HH}$ 15.3 Hz, H_B NCH_2), 4.97 d (1H, $^2J_{HH}$ 15.3 Hz, H_A NCH_2), 5.33 s (1H, 1-H), 7.08–7.36 m (9H, H_{arom}), 7.52 m (1H, 7-H), 7.80–7.90 m (2H, 5-H, 6-H), 8.01 d.d (1H, 8-H)
XIId	1609 (C=C); 1658 (C^9=O); 1715 (C^3=O)	3.92 d (1H, $^2J_{HH}$ 15.3 Hz, H_B NCH_2), 4.94 d (1H, $^2J_{HH}$ 15.3 Hz, H_A NCH_2), 5.44 s (1H, 1-H), 7.13–7.39 m (9H, H_{arom}), 7.52 m (1H, 7-H), 7.80–7.90 m (2H, 5-H, 6-H), 8.01 d.d (1H, 8-H)
XIIIa	1611 (C=C); 1653 (C^9=O); 1708 (C^3=O)	2.69 m (1H, H_B NCH_2), 2.84–3.02 m (2H, CH_2Ph), 3.90 m (1H, H_A NCH_2), 5.54 s (1H, 1-H), 7.10–7.40 m (10H, H_{arom}), 7.52 m (1H, 7-H), 7.69–7.90 m (2H, 5-H, 6-H), 8.02 d.d (1H, 8-H)
XIIId	1609 (C=C); 1659 (C^9=O); 1710 (C^3=O)	2.75 m (1H, H_B NCH_2), 2.86–3.02 m (2H, CH_2Ph), 3.94 m (1H, H_A NCH_2), 5.59 s (1H, 1-H), 7.12–7.42 m (9H, H_{arom}), 7.52 m (1H, 7-H), 7.69–7.90 m (2H, 5-H, 6-H), 8.02 d.d (1H, 8-H)
XIIIf	1611 (C=C); 1650 (C^9=O); 1712 (C^3=O)	2.74 m (1H, H_B NCH_2), 2.86–3.03 m (2H, CH_2Ph), 3.75 s (3H, OCH_3), 3.88 m (1H, H_A NCH_2), 5.47 s (1H, 1-H), 6.87 d (2H, H_{arom}), 7.13–7.29 m (7H, H_{arom}), 7.51 m (1H, 7-H), 7.69–7.90 m (2H, 5-H, 6-H), 8.01 d.d (1H, 8-H)
XIVa	1608 (C=C); 1654 (C^9=O); 1709 (C^3=O)	3.88 d (1H, $^2J_{HH}$ 15.9 Hz, H_B NCH_2), 4.95 d (1H, $^2J_{HH}$ 15.9 Hz, H_A NCH_2), 5.46 s (1H, 1-H), 6.22 m (1H, furyl), 6.34 m (1H, furyl), 7.28–7.40 m (5H, H_{arom}), 7.49–7.58 m (2H, 7-H, 1H, furyl), 7.79–7.90 m (2H, 5-H, 6-H), 8.01 d.d (1H, 8-H)
XIVb	1608 (C=C); 1652 (C^9=O); 1716 (C^3=O)	2.33 s (3H, CH_3), 3.83 d (1H, $^2J_{HH}$ 15.9 Hz, H_B NCH_2), 4.95 d (1H, $^2J_{HH}$ 15.9 Hz, H_A NCH_2), 5.40 s (1H, 1-H), 6.23 m (1H, furyl), 6.35 m (1H, furyl), 7.15–7.20 m (4H, H_{arom}), 7.48–7.56 m (2H, 7-H, 1H, furyl), 7.79–7.90 m (2H, 5-H, 6-H), 8.01 d.d (1H, 8-H)
XIVd	1609 (C=C); 1653 (C^9=O); 1715 (C^3=O)	3.97 d (1H, $^2J_{HH}$ 15.8 Hz, H_B NCH_2), 4.92 d (1H, $^2J_{HH}$ 15.8 Hz, H_A NCH_2), 5.49 s (1H, 1-H), 6.22 m (1H, furyl), 6.33 m (1H, furyl), 7.32–7.40 m (4H, H_{arom}), 7.49–7.58 m (2H, 7-H, 1H, furyl), 7.79–7.90 m (2H, 5-H, 6-H), 8.01 d.d (1H, 8-H)

[a] Strong absorption bands in the region 1590–1750 cm^{-1} are given.

crystallization. The yield of the final product also depends on the substituent in the benzene ring of the initial aromatic aldehyde. Electron-withdrawing substituents favor formation of chromenopyrroles, while aromatic aldehydes with electron-donating groups gave lower yields.

The structure of the isolated compounds was confirmed by their IR and ^1H NMR spectra and elemental analyses. The IR spectra of 1,2-dihydrochromeno[2,3-*c*]pyrrole-3,9-diones in KBr characteristically contained three absorption bands in the region 1590–1720 cm^{-1}: a medium-intensity band at 1600–1620 cm^{-1} due to stretching vibrations of the C=C bond, a strong band at 1640–1665 cm^{-1} belonging to stretching vibrations of the C^9=O carbonyl, and a strong carbonyl band at 1695–1720 cm^{-1} (C^3=O). The intensity ratio and position of these bands depend on the substituents, but the general pattern remains the same for all compounds (Table 2). No absorption was observed in the region 3200–3600 cm^{-1}, indicating participation of the OH and NH in the cyclocondensation. In the ^1H NMR spectra of **IX–XIV** (Table 2), the 1-H proton resonated as a singlet at δ 6.30–6.70 ppm. The 5-H and 6-H protons gave rise to a multiplet in the region δ 7.75–7.95 ppm, the 7-H signal was a doublet of doublets at δ 7.50–7.60 ppm, and the doublet at δ 8.00–8.10 ppm was assigned to 8-H. Diastereotopic protons in the methylene group on the N^2 nitrogen atom gave two multiplets (**X**, **XI**, **XIII**) or two doublets (**XII**, **XIV**).

Chromone derivatives **IX–XIV** are colorless crystalline substances that are readily soluble in acetic

acid, dioxane, acetonitrile, chloroform, and methylene chloride and sparingly soluble in alcohols. All these compounds were synthesized from accessible reagents. Obviously, the conditions of synthesis and isolation procedure can be optimized for each particular compound if necessary.

Thus three-component condensation of methyl 4-(*o*-hydroxyphenyl)-2,4-dioxobutanoate, aromatic aldehyde, and aliphatic amine provides a convenient one-pot procedure for the synthesis of a number of previously unknown 2-alkyl-1-aryl-1,2-dihydrochromeno[2,3-*c*]pyrrole-3,9-diones that attract interest as potential biologically active substances. The scope of the described modified three-component cyclocondensation will be considered elsewhere.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Perkin–Elmer Spectrum One spectrometer with a resolution of 1 cm^{-1} (12 scans). The ^1H NMR spectra were measured on a Varian VXR-300 instrument from solutions in DMSO-d_6 using hexamethyldisiloxane as internal reference.

General procedure for the synthesis of 2-alkyl-1-aryl-1,2-dihydrochromeno[2,3-*c*]pyrrole-3,9-diones IX–XIV. *a*. A mixture of 0.01 mol of benzaldehyde and 0.01 mol of the corresponding aliphatic amine in 15 ml of anhydrous ethanol (96% ethanol, methanol, or propan-2-ol) was heated to 50°C and was left to stand for 15 min, 0.01 mol of methyl 4-(*o*-hydroxyphenyl)-2,4-dioxobutanoate was added, and the mixture was heated under reflux over a period indicated in Table 1, cooled, and left to stand in a refrigerator for several days until crystallization. The precipitate (compound **IXa**, **XIIa**, or **XIVa**) was filtered off, washed with the corresponding solvent, and purified by recrystallization from ethanol.

b. Aromatic aldehyde **IIa**–**IIg**, 0.01 mol, was dissolved in 12 ml of anhydrous ethanol, 0.01 mol of aliphatic amine **III**–**VIII** was added, and the mixture was heated to 50°C and left to stand for 15 min. Methyl 4-(*o*-hydroxyphenyl)-2,4-dioxobutanoate, 0.01 mol, was added to the warm mixture (30°C), the mixture was stirred for 30 min at 30–35°C, quickly heated to the boiling point, and kept boiling for 5 min, 7 ml of glacial acetic acid was added, and the mixture was heated for 30 min under reflux and cooled. The precipitate (compound **IX**–**XIV**) was filtered off and recrystallized from appropriate solvent. The yields, melting points, and elemental analyses of compounds **IX**–**XIV** are given in Table 3. Samples of **IXa**, **XIIa**, and **XIVa** obtained by the two methods (*a* and *b*) showed no depression of the melting point on mixing.

The filtrate obtained after separation of compound **IXa** (method *b*) was combined with the mother liquor that remained after recrystallization of **IXa**. Volatile substances were removed under reduced pressure, the residue was dissolved in 20 ml of toluene, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (40–70 μm) using chloroform–methanol (0 to 5% of the latter) as eluent (gradient elution) to isolate 0.35 g (12%) of compound **IXa**, 0.12 g (5.35%) of **XIXa**, 0.11 g (4.9%) of **XXIIIa**, 0.09 g (2.88%) of **XXIVa**, 0.1 g (4.9%) of **XXV**, and 0.11 g (5.42%) of **XXVIa**.

Likewise, from the filtrates obtained after separation of **XIIa**, we isolated the following compounds: **XIIa**, 0.62 g (15.7%); **XIXa**, 0.11 g (4.9%); **XXIId**, 0.27 g (10.4%); **XXIIIa**, 0.14 g (6.25%); **XXIVa**, 0.17 g (5.5%); **XXV**, 0.11 g (5.4%); **XXVId**, 0.16 g (5.7%).

Likewise, from the filtrates obtained after separation of **XIIb**, we isolated the following compounds: **XIIb**, 0.63 g (16.3%); **XIXb**, 0.12 g (5.04%); **XXIId**, 0.29 g (10.8%); **XXIIIb**, 0.15 g (6.3%); **XXIVb**, 0.12 g (3.53%); **XXV**, 0.13 g (6.37%); **XXVId**, 0.15 g (5.37%).

1-(2-Hydroxyphenyl)-3-phenylprop-2-en-1-one (XIXa) was isolated by column chromatography from the filtrates obtained after separation of compounds **IXa** and **XIIa**. Yellow crystals, mp 88–89°C. Compound **XIXa** was identical as the condensation product of benzaldehyde with *o*-hydroxyacetophenone [6] in the melting points and IR and ^1H NMR spectra.

1-(2-Hydroxyphenyl)-3-(4-methylphenyl)prop-2-en-1-one (XIXb) was isolated from the filtrates obtained after separation of compound **XIIb**. Yellow crystals, mp 71°C. Compound **XIXb** was identical as the condensation product of 4-methylbenzaldehyde with *o*-hydroxyacetophenone [7] in the melting points and IR and ^1H NMR spectra.

***N*,*N*′-Dibenzylethanediamide (XXIId)** was isolated from the filtrates obtained after separation of compounds **XIIa** and **XIIb**. mp 221–222°C (from ethanol). IR spectrum, ν, cm^{-1}: 1653 (C=O); 3280 (NH). ^1H NMR spectrum, δ, ppm: 4.33 d (4H, CH_2, $^3J_{HH}$ = 6.6 Hz), 7.19–7.32 m (10H, H_{arom}), 9.23 t (2H,

NH, $^3J_{HH}$ = 6.6 Hz). Found, %: C 71.47; H 5.92; N 10.62. $C_{16}H_{16}N_2O_2$. Calculated, %: C 71.62; H 6.01; N 10.44. Compound **XXIId** showed no depression of the melting point on mixing with a sample prepared as described in [8].

2-Phenyl-2,3-dihydro-4*H*-chromen-4-one (XXIIIa) was isolated from the filtrates obtained after separation of compounds **IXa** and **XIIa**. mp 75–76°C (from aqueous propan-2-ol) [6, 9]. ^{1}H NMR spectrum, δ, ppm: 2.85 d.d (1H), 3.28 d.d (1H), 5.67 d.d (1H, 2-H), 7.08–7.12 m (2H, H_{arom}), 7.39–7.62 m (6H, H_{arom}), 7.79 d.d (1H, 5-H). Found, %: C 80.21; H 5.43. $C_{15}H_{12}O_2$. Calculated, %: C 80.34; H 5.39. Compound **XXIIIa** showed no depression of the melting point on mixing with a sample prepared as described in [6].

2-(4-Methylphenyl)-2,3-dihydro-4*H*-chromen-4-one (XXIIIb) was isolated from the filtrates obtained after separation of compound **XIIb**. mp 71–72°C (from aqueous propan-2-ol) [9]. ^{1}H NMR spectrum, δ, ppm: 2.32 s (3H, CH_3), 2.81 d.d (1H), 3.24 d.d (1H),

Table 3. Yields, melting points, and elemental analyses of 2-alkyl-1-aryl-1,2-dihydrochromeno[2,3-*c*]pyrrole-3,9-diones **IX**–**XIV**

Comp. no.	Yield,[a] %	mp, °C (solvent)	Found, %			Formula	Calculated, %		
			C	H	N(Cl)		C	H	N(Cl)
IXa	55[b]	247–248 (DMF–ethanol, 1:4)	74.02	4.58	4.93	$C_{18}H_{13}NO_3$	74.22	4.50	4.81
IXb	50	237–238 (acetonitrile)	74.62	5.03	4.48	$C_{19}H_{15}NO_3$	74.74	4.95	4.59
IXc	56	234–235 (DMF–ethanol, 1:3)	70.06	3.87	4.69	$C_{18}H_{12}FNO_3$	69.90	3.91	4.53
IXd	57	248–249 (DMF–ethanol, 1:2)	66.52	3.59	(10.97)	$C_{18}H_{12}ClNO_3$	66.37	3.71	(10.88)
IXe	59	222–224 (DMF–ethanol, 1:1)	64.43	3.64	8.51	$C_{18}H_{12}N_2O_5$	64.29	3.60	8.33
IXf	44	265–266 (DMF–propan-2-ol, 1:3)	70.91	4.77	4.49	$C_{19}H_{15}NO_4$	71.02	4.71	4.36
IXg	38	223–224 (ethanol)	68.52	4.63	4.07	$C_{20}H_{17}NO_5$	68.37	4.68	3.94
Xa	49	232–233 (DMF–ethanol, 1:5)	74.83	4.89	4.70	$C_{19}H_{15}NO_3$	74.74	4.95	4.59
Xe	52	233–234 (DMF–ethanol, 1:2)	64.98	4.11	7.93	$C_{19}H_{14}N_2O_5$	65.14	4.03	8.00
Xf	43	267–268 (acetonitrile)	71.70	5.13	4.32	$C_{20}H_{17}NO_4$	71.63	5.11	4.18
XIa	37	195–196 (ethanol)	71.49	5.18	4.29	$C_{20}H_{17}NO_4$	71.63	5.11	4.18
XIc	42	197–198 (ethanol)	68.14	4.60	4.11	$C_{20}H_{16}FNO_4$	67.98	4.56	3.96
XIf	32	203–204 (ethanol)	69.16	5.30	4.01	$C_{21}H_{19}NO_5$	69.03	5.24	3.83
XIIa	47[b]	242–243 (dioxane)	78.61	4.72	3.95	$C_{24}H_{17}NO_3$	78.46	4.66	3.81
XIIb	49[b]	232–233 (DMF–ethanol, 1:3)	78.74	5.06	3.80	$C_{25}H_{19}NO_3$	78.72	5.02	3.67
XIIc	57	271–272 (DMF–ethanol, 1:2)	74.72	4.26	3.71	$C_{24}H_{16}FNO_3$	74.80	4.18	3.63
XIId	61	279–280 (DMF–ethanol, 1:1)	71.80	4.08	(8.76)	$C_{24}H_{16}ClNO_3$	71.73	4.01	(8.82)
XIIIa	47	214–215 (DMF–ethanol, 1:4)	78.61	5.07	3.71	$C_{25}H_{19}NO_3$	78.72	5.02	3.67
XIIId	44	202–203 (DMF–ethanol, 1:3)	71/95	4/32	(8/61)	$C_{25}H_{18}ClNO_3$	72/20	4/36	(8/52)
XIIIe	38	178–179 (acetonitrile)	75.81	5.15	3.52	$C_{26}H_{21}NO_4$	75.90	5.14	3.40
XIVa	61	219–220 (DMF–ethanol, 1:4)	74.02	4.20	3.98	$C_{22}H_{15}NO_4$	73.94	4.23	3.92
XIVb	40	220–221 (DMF–ethanol, 1:5)	74.31	4.70	3.85	$C_{23}H_{17}NO_4$	74.38	4.61	3.77
XIVd	52	252–253 (DMF–ethanol, 1:3)	67.32	3.69	(9.14)	$C_{22}H_{14}ClNO_4$	67.44	3.60	(9.05)

[a] Method *b*. [b] After crystallization. The overall yield with account taken of the amount isolated by chromatography was 67% (**IXa**), 62.7% (**XIIa**), 65.5% (**XIIb**).

5.61 d.d (1H, 2-H), 7.07–7.12 m (2H, H_{arom}), 7.23 d (2H, H_{arom}), 7.42 d (2H, H_{arom}), 7.58 m (1H, 7-H), 7.79 d.d (1H, 5-H). Found, %: C 80.49; H 5.83. $C_{16}H_{14}O_2$. Calculated, %: C 80.65; H 5.92.

3-Benzylidene-2-phenyl-2,3-dihydro-4*H*-chromen-4-one (XXIVa) was isolated from the filtrates obtained after separation of compounds **IXa** and **XIIa**. mp 146–147°C (from ethanol) [10]. IR spectrum, ν, cm^{-1}: 1607 (C=C), 1676 (C=O). ^1H NMR spectrum, δ, ppm: 6.63 s (1H, 2-H), 6.94–7.07 m (2H, H_{arom}), 7.32–7.61 m (11H, H_{arom}), 7.71 d.d (1H, 5-H), 7.96 s (1H, CH=). Found, %: C 84.71; H 5.13. $C_{22}H_{16}O_2$. Calculated, %: C 84.59; H 5.16.

3-(4-Methylbenzylidene)-2-(4-methylphenyl)-2,3-dihydro-4*H*-chromen-4-one (XXIVb) was isolated from the filtrates obtained after separation of compound **XIIb**. mp 126–127°C (from ethanol). IR spectrum, ν, cm^{-1}: 1605 (C=C), 1672 (C=O). ^1H NMR spectrum, δ, ppm: 2.27 s (3H, CH_3), 2.23 s (3H, CH_3), 6.61 s (1H, 2-H), 6.94–7.04 m (2H, H_{arom}), 7.14–7.31 m (8H, H_{arom}), 7.47 m (1H, 7-H), 7.77 d.d (1H, 5-H), 7.94 s (1H, CH=). Found, %: C 84.56; H 6.01. $C_{24}H_{20}O_2$. Calculated, %: C 84.68; H 5.92.

Methyl 4-oxo-4*H*-chromene-2-carboxylate (XXV) was isolated from the filtrates obtained after separation of compounds **IXa**, **XIIa**, and **XIIb**. mp 119–120°C (from aqueous ethanol) [3]. IR spectrum, ν, cm^{-1}: 1656 (C^4=O), 1737 (C=O). ^1H NMR spectrum, δ, ppm: 3.93 s (3H, CH_3O), 6.92 s (1H, 3-H), 7.53 m (1H, 6-H), 7.72 d.d (1H, 8-H), 7.87 m (1H, 7-H), 8.03 d.d (1H, 5-H). Found, %: C 64.56; H 4.03. $C_{11}H_8O_4$. Calculated, %: C 64.71; H 3.95.

***N*-Methyl-4-oxo-4*H*-chromene-2-carboxamide (XXVIa)** was isolated from the filtrate obtained after separation of compound **IXa**. mp 223–224°C (from ethanol) [11]. IR spectrum, ν, cm^{-1}: 1607 (C=C), 1642 (C^4=O), 1690 (C=O), 3190 (NH). ^1H NMR spectrum, δ, ppm: 2.87 d (3H, CH_3N), 6.78 s (1H, 3-H), 7.49 m (1H, 6-H), 7.68 d.d (1H, 8-H), 7.83 m (1H, 7-H), 8.03 d.d (1H, 5-H), 8.99 br.q (1H, NH). Found, %: C 65.14; H 4.52; N 7.01. $C_{11}H_9NO_3$. Calculated, %: C 65.02; H 4.46; N 6.89.

***N*-Benzyl-4-oxo-4*H*-chromene-2-carboxamide (XXVId)** was isolated from the filtrates obtained after separation of compounds **XIIa** and **XIIb**. mp 181–183°C (from ethanol) [12]. ^1H NMR spectrum, δ, ppm: 4.37 d (2H, CH_2N), 6.78 s (1H, 3-H), 7.15–7.51 m (6H, H_{arom}), 7.67 d.d (1H, 8-H), 7.83 m (1H, 7-H), 8.03 d.d (1H, 5-H), 9.21 br.s (1H, NH). Found, %: C 72.96; H 4.62; N 5.12. $C_{17}H_{13}NO_3$. Calculated, %: C 73.11; H 4.69; N 5.01.

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