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Azines and Azoles: CXXIV.[1] New Synthesis of 2-Oxochromene-3-carboxamides

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Abstract — 2-Aryl-4-hydroxy-6*H*-1,3-thiazin-6-ones react with substituted 2-hydroxybenzaldehydes in polar solvents to give *N*-arylcarbothioyl-2-oxochromene-3-carboxamides in 60–70% yield.
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We previously showed that 2-substituted 4,6-dihydroxy(oxo)pyrimidines react with aromatic aldehydes to give bis(4,6-dihydroxypyrimidin-5-yl)arylmethanes which undergo intramolecular cyclization to the corresponding 5*H*-pyrano[2,3-*d*:6,5-*d*']dipyrimidine derivatives on heating in a mixture of acetic anhydride with acetic acid [2–4]. If a nucleophilic group (such as OH or NH_2) is present in the molecule of the carbonyl component in the ortho position with respect to the carbonyl group, a different set of products is formed. For example, in the condensation of 4,6-dihydroxypyrimidines with substituted salicylaldehydes, apart from bis(4,6-dihydroxypyrimidin-5-yl)-(2-hydroxyphenyl)methanes, we isolated *N*-formyl-2-oxochromene-3-carboxamides, 2-oxochromene-3-carboxamides, and 4*H*-chromeno[4,3-d]pyrimidines which were formed via intramolecular cyclization as a result of attack by the phenolic hydroxy group on the C^4=O carbonyl carbon atom in the pyrimidine ring [5, 6]. Unlike 4,6-dihydroxypyrimidines, their thia analogs, 4-hydroxy-6-oxo-1,3-thiazines, are known to react with aromatic aldehydes to give substituted 4,5-dihydropyrano[2,3-d][1,3]thiazines [7]. Reactions of hydroxythiazinones with aldehydes having a nucleophilic substituent in the ortho position with respect to the carbonyl group were not studied previously. Taking into account strong differences in the behavior of 4,6-dihydroxypyrimidines and 4-hydroxy-6-oxo-1,3-thiazines and the results of reactions of polyhydroxypyrimidines and some their analogs with carbonyl compounds, we thought it to be reasonable to examine reactions of 2-aryl-4-hydroxy-6*H*-1,3-thiazin-6-ones **I** with substituted salicylaldehydes.

We have found that the reactions of 2-aryl-4-hydroxy-6*H*-1,3-thiazin-6-ones **I** with substituted 2-hydroxybenzaldehydes **II** lead to the formation of *N*-arylcarbothioyl-2-oxochromene-3-carboxamides **IIIa**–**IIIf** in 60–70% yield (Scheme 1, Table 1), regardless of the nature and position of substituent in the thiazine ring or aldehyde molecule and reaction conditions (temperature, reaction time, and reactant ratio).

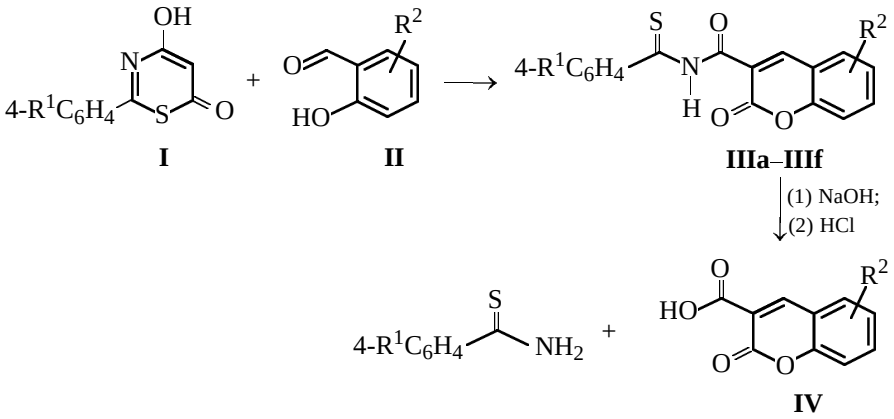
The reactions were carried out in polar aprotic (DMSO, pyridine) and protic solvents (alcohols). The yield of compounds **III** in alcohols was considerably lower, presumably due to concurrent nucleophilic cleavage of the thiazine ring by the solvent. Compounds **III** were formed in very poor yields (3–5%) when the reactions were carried out in nonpolar solvents (1,4-dioxane, toluene). The condensation also occurred (yield 20–40%) when the reactants were heated at 130–140°C under solvent-free conditions.

The formation of just *N*-arylcarbothioyl-2-oxochromene-3-carboxamides **III** follows from the fact that alkaline hydrolysis of compound **IIIa** (10% aqueous NaOH, 60°C, 10 min) afforded almost quantitatively 2-oxochromene-3-carboxylic acid (**IV**) and thiobenzamide, whose properties and spectral parameters coincided with those reported previously [8].

The structure of compounds **IIIa**–**IIIf** was confirmed by the ^{1}H and ^{13}C NMR, IR, UV, and mass spectra. The fragmentation of chromenecarboxamides **IIIa**–**IIIf** under electron impact (Table 2) follows the general pattern depicted in Scheme 2. All these compounds give rise to the molecular ion whose further fragmentation can take several pathways: formation of substituted coumarin via elimination of $ArC{\equiv}S^+$ and HNCO (pathway *a*) or successive elimination of $ArC{\equiv}NH^+$, S, and CO (pathway *b*). In addition, intramolecular cyclization to chromenothiazine is possible

[1] For communication CXXIII, see [1].

Scheme 1.



III, R^1 = H, R^2 = H (**a**), 8-MeO (**b**), 7-HO (**c**); R^1 = MeO, R^2 = H (**d**), 7-HO (**e**), 6-O2N (**f**).

(pathway *c*) with subsequent elimination of ArC≡N, CO, and S to give substituted coumarin.

The ^{1}H and ^{13}C NMR spectra of 2-oxochromene-3-carboxamides **III** resemble those of previously reported *N*-formyl-2-oxochromene-3-carboxamides [5] and unsubstituted 2-oxochromene-3-carboxylic acid (**IV**) (Tables 3, 4). Their ^{1}H NMR spectra contain signals from the NH proton (δ 12.5–13.1 ppm), 4-H (δ 8.8–9.2 ppm), and aromatic protons in the fused

Table 1. Yields, melting points, R_f values, and elemental analyses of *N*-(arylcarbothioyl)-2-oxochromene-3-carboxamides **IIIa**–**IIIf**

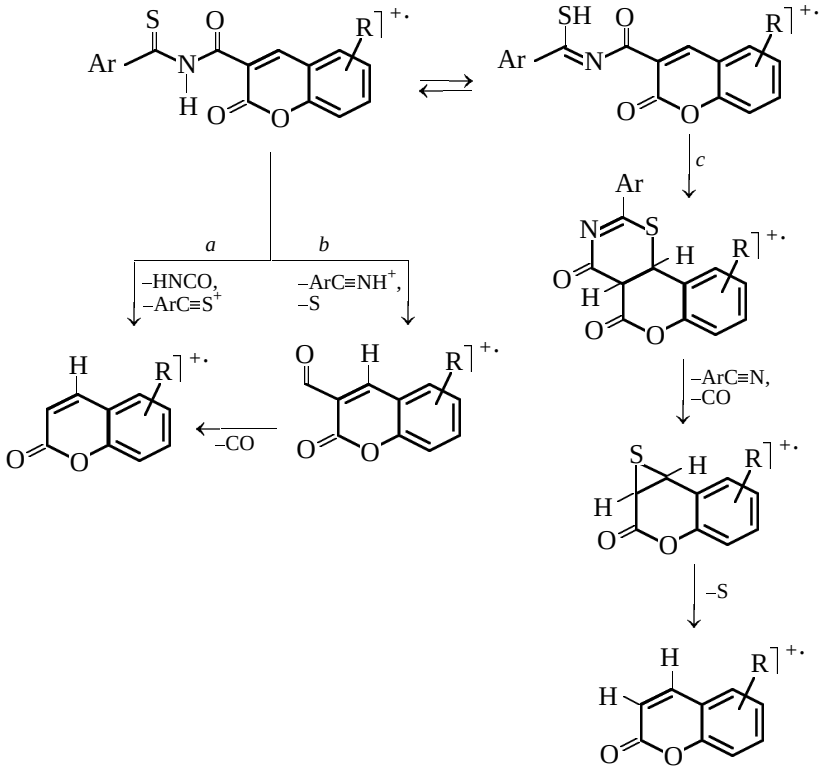
Comp. no.	Yield,[a] %	mp, °C[b]	R_f[c]	Found, %				Formula	Calculated, %			
				C	H	N	S		C	H	N	S
IIIa	78	218–220	0.42 (A)	64.0	3.4	4.3	10.5	$C_{17}H_{11}NO_3S$	66.0	3.5	4.5	10.4
IIIb	63	245–247	0.27 (A)	64.0	3.5	4.2	9.9	$C_{18}H_{13}NO_4S$	63.7	3.8	4.1	9.5
IIIc	65	>300	0.11 (B)	63.1	3.5	4.6	9.7	$C_{17}H_{11}NO_4S$	62.8	3.7	4.3	9.8
IIId	60	232–234	0.30 (A)	64.1	3.6	4.0	9.7	$C_{18}H_{13}NO_4S$	63.7	3.8	4.1	9.5
IIIe	61	>300	0.08 (B)	61.5	4.0	3.6	8.7	$C_{18}H_{13}NO_5S$	60.8	3.7	3.9	9.0
IIIf	60	205–207	0.14 (A)	54.6	3.4	7.2	8.5	$C_{18}H_{12}N_2O_6S$	56.7	3.1	7.3	8.3

[a] In pyridine. [b] Compounds **IIIa, IIId**, and **IIIf** were recrystallized from ethanol, and **IIIb, IIIc**, and **IIIe**, from glacial acetic acid. [c] Eluent chloroform (A) or acetone–hexane, 1:3 (B).

Table 2. Mass spectra of compounds **IIIa, IIIb, IIId**, and **IIIf**, *m/z* (I_{rel}, %)

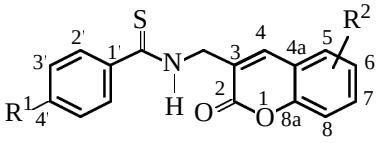
Comp. no.	M^+	$[M-ArCN-CO]^+$	$[M-ArCNH]^+$	$[M-ArCN-CO-S]^+$	$[M-ArCS+-HNCO]^+$	Other ions
IIIa	309 (45)	178 (15)	173 (100)	146 (7)	145 (8)	121 (14), 104 (20), 103 (11)
IIIb	339 (27)	208 (10)	203 (100)	176 (11)	175 (5)	121 (20), 104 (10), 103 (15)
IIId	339 (20)	178 (6)	173 (100)	146 (5)	145 (2)	151 (19), 134 (18), 133 (18)
IIIf	384 (7)	223 (8)	218 (17)	191 (15)	190 (6)	151 (19), 134 (20), 133 (100)

Scheme 2.



benzene ring and thiobenzoyl group (δ 6.6–8.2 ppm). In the ^{13}C NMR spectra (Table 4), characteristic signals are those belonging to the amide carbonyl (δ_C 159–161 ppm) and thiocarbonyl carbon atoms (δ_C 198–202 ppm), carbon atoms in the pyran ring (δ_C 160–165, 111–118, and 149–150 ppm for C^2, C^3, and C^4, respectively), and aromatic carbon atoms (δ_C 112–158 ppm). The ^1H and ^{13}C NMR spectra lack signals assignable to the exocyclic carbon atoms and protons attached thereto in aryldihetarylmethanes (C–H) or arylmethylidenethiazines (C^5=C–H), which usually appear at about δ_C 29 or 100 ppm and δ 6 or 8 ppm, respectively. Signals typical of C^5H in initial 1,3-thiazines (δ_C 90, 5 ppm) were also absent.

Table 3. ^1H NMR spectra of compounds **IIIa**–**IIIf** and **IV**, δ, ppm [a]



Comp. no.	NH (1H)	C^4H (1H)	C^5H (1H)	C^6H (1H)	C^7H (1H)	C^8H (1H)	$C^{2'}H$, d (2H)	$C^{3'}H$, d (2H)	$C^{4'}H$, d.d (1H)	OCH_3, s (3H)	OH, s (1H)
IIIa	12.91 s	8.98 s	8.04 d	7.44 d.d	7.78 d.d	7.53 d	7.48	7.92	7.54	–	–
IIIb	12.89 s	8.94 s	7.61 d	7.43 d	7.56 d	–	7.83	7.50	7.55	3.96	–
IIIc	12.92 s	8.93 s	7.89 d	6.94 d	–	6.86 s	7.82	7.48	7.59	–	11.34
IIId	12.75 s	8.99 s	8.02 d	7.45 d.d	7.76 d.d	7.53 d	7.91	7.02	–	3.86	–
IIIe	12.78 s	8.93 s	7.87 s	6.94 d	–	6.86 s	7.90	7.03	–	3.85	11.35
IIIf	12.60 s	9.13 s	8.70 s	–	8.58 d	7.64 d	7.97	6.95	–	3.86	–
IV	–	8.74 s	7.90 d	7.40 d.d	7.72 d.d	7.43 d	–	–	–	–	–

[a] The spectra of **IIIa, IIIb, IIId**, and **IIIf** were recorded in $CDCl_3$, and of **IIIc** and **IIIe**, in DMSO-d_6.

Table 4. ^{13}C NMR spectra of compounds **IIIa**–**IIIf** and **IV**, δ_C, ppm[a]

Comp. no.	C=O	C=S	C^2=O	C^3	C^4	C^{4a}	C^5	C^6	C^7	C^8	C^{8a}	$C^{1'}$	$C^{2'}$	$C^{3'}$	$C^{4'}$	OCH_3
IIIa	160.2	200.9	160.6	118.3	149.1	119.6	130.5	125.4	134.9	116.3	153.9	142.1	127.3	128.3	132.1	–
IIIb	159.9	202.4	160.6	118.9	149.3	119.8	125.4	121.4	143.2	116.9	146.3	142.1	127.3	128.3	132.1	56.3
IIIc	161.2	202.0	164.8	111.3	150.4	113.3	132.6	114.8	156.6	101.9	160.3	142.2	127.2	128.3	131.9	–
IIId	160.2	200.2	162.9	118.4	149.3	119.4	130.5	125.3	134.8	116.2	153.9	160.4	113.5	129.8	134.4	55.5
IIIe	162.9	200.0	164.7	111.3	150.2	113.4	132.6	114.8	156.6	101.9	161.3	160.3	113.6	129.8	134.5	55.6
IIIf	160.3	198.9	163.6	118.3	150.1	120.5	129.3	125.8	144.9	118.5	157.4	158.2	113.9	129.7	134.8	55.6
IV	156.6	–	163.8	117.9	148.2	118.3	130.1	124.7	134.2	116.0	154.4	–	–	–	–	–

[a] The spectra of **IIIa, IIIb, IIId**, and **IIIf** were recorded in $CDCl_3$, and of **IIIc** and **IIIe**, in DMSO-d_6. For atom numbering, see Table 3.

Table 5. UV and IR spectra of 2-oxochromene-3-carboxamides **IIIa**–**IIIf**

Comp. no.	UV spectrum		IR spectrum (KBr), ν, cm^{-1}			
	λ_{max}, nm	log ε	NH	$C^2(=O)O$	C=O	C^2OC^{8a}
IIIa	300	4.25	3150, 3450	1730	1560, 1620	1200, 1250
IIIb	322	4.19	3150, 3400	1720	1540, 1630	1190, 1250
IIIc	325	4.23	3150, 3430	1710	1550, 1630	1180, 1250
IIId	310	4.21	3150, 3420	1710	1510, 1610	1180, 1230
IIIe	321	4.23	3150, 3450	1730	1520, 1620	1170, 1250
IIIf	318	4.20	3180, 3430	1740	1550, 1620	1180, 1250

Crystalline compounds **III** showed in the IR spectra (Table 5) absorption bands due to stretching vibrations of the imide NH group (~3400 cm^{-1}), lactone moiety O=C–O–C (1710–1740, 1240–1250, and 1100–1250 cm^{-1}), and amide group (1620–1640 cm^{-1}, amide **I**; 1560–1570 cm^{-1}, amide **II**); analogous absorption pattern was observed in the spectra of 2-oxochromene-3-carboxamide, its *N*-formyl derivative, and 2-oxochromene-3-carboxylic acid [5, 9]. Unlike the initial 1,3-thiazines, the UV spectra of compounds **III** in ethanol contained only one absorption maximum at λ 300–320 nm (as in the UV spectra of 2-oxochromene-3-carboxamide and its *N*-formyl derivative [5]).

It is reasonable to presume that the formation of chromene system (Scheme 3) in the reaction of thiazines **I** with salicylaldehydes **II** involves aryl(2-aryl-4-hydroxy-6-oxo-6*H*-1,3-thiazin-5-yl)methanols **V** as intermediate, the more so analogous carbinols were isolated from the reaction mixtures obtained from thiazines **I** and benzaldehydes having no nucleophilic groups [7]. With a view to interpret the experimental data, we performed PM3 quantumchemical calculations of the charges on atoms, energies of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO), and the corresponding orbital coefficients of 2-aryl-1,3-thiazines **I**, their anions, aldehydes **II**, and carbinols **V** (Table 6–8). The results showed that the substituent in the benzene ring on C^2 almost does not affect the charge on C^5 (reaction center) in molecules **I** (Table 6). However, it exerts an appreciable effect on the HOMO energy and the contribution of C^5 to the HOMO. Electron-donor substituents increase the HOMO energy, so that it becomes closer to the LUMO energy of aldehyde **II**, while electron-acceptor substituent reduce the HOMO energy thus enlarging the energy gap between the HOMO of **I** and LUMO of **II**.

As might be expected, the negative charge on C^5 sharply increases in going from neutral thiazine **I** molecule to the corresponding anion; also, the contribution of C^5 AO to the HOMO and the HOMO energy increase. The same tendency is observed for salicylaldehydes: the substituent therein only slightly affects the positive charge on the carbonyl carbon atom, but strongly influences its contribution to the LUMO and the LUMO energy (Table 7).

These data led us to presume that the formation of

Scheme 3.

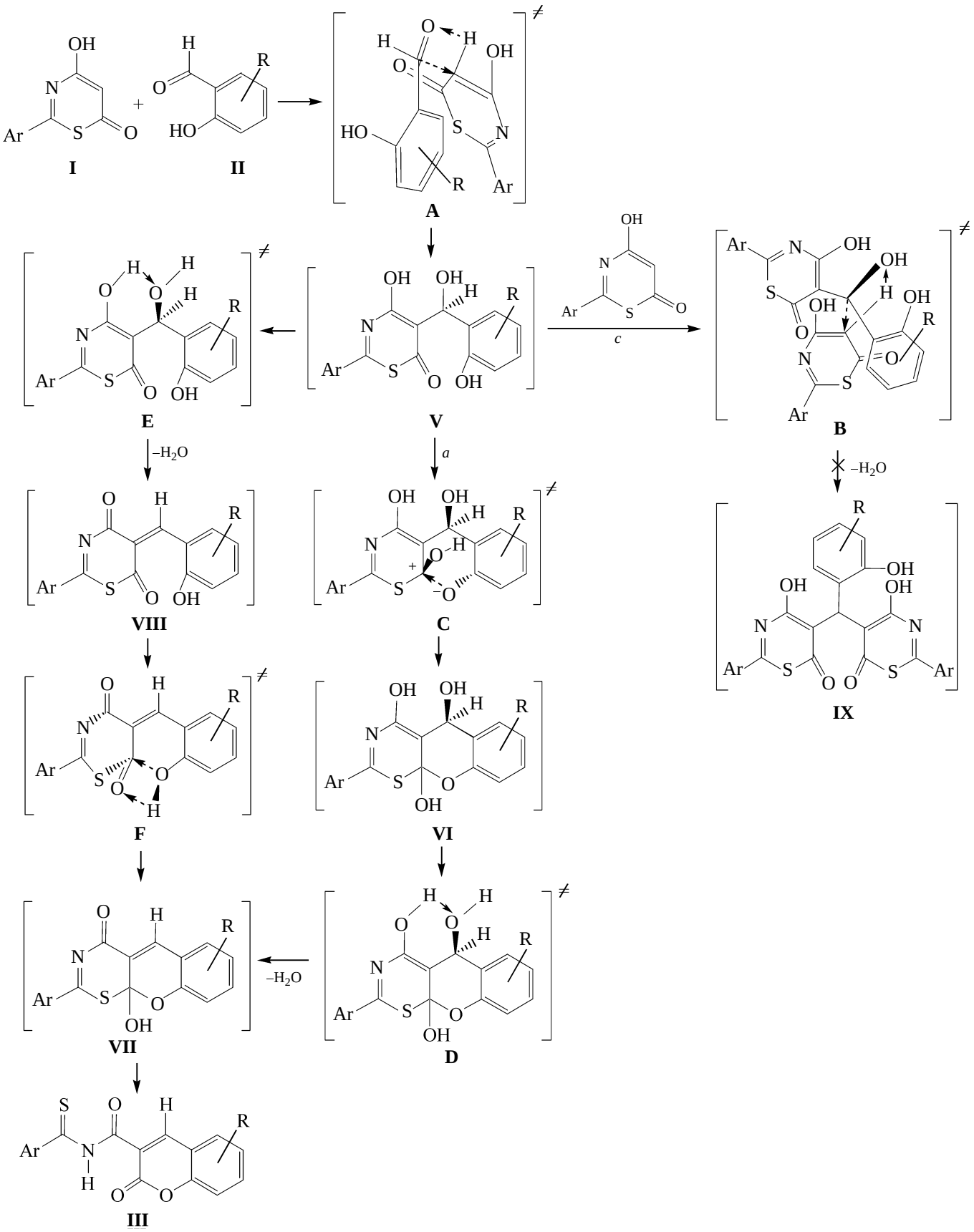


Table 6. HOMO energies, charges on atoms (*q*), and orbital coefficients (*c*) of 2-aryl-1,3-thiazines **I** and their anions

Comp. no.	R^1	$-E_{HOMO}$, eV		$-q(C^5)$		$c(C^5)$	
		compound **I**[a]	anion	compound **I**[a]	anion	compound **I**[a]	anion
Ia	4-Me_2N	8.26	4.38	0.42	0.62	–0.16	–0.90
Ib	4-MeO	9.23	4.47	0.41	0.62	0.32	–0.72
Ic	H	9.61	4.48	0.41	0.62	–0.47	0.78
Id	4-Cl	9.46	4.57	0.41	0.62	0.33	0.83
Ie	4-O_2N	10.14	4.86	0.39	0.61	0.51	–0.77

[a] Neutral molecule.

carbinols **V** from 1,3-thiazines **I** and aldehydes **II** is an orbital-controlled process. This is consistent with the experimental data. The fact that the reaction of thiazines **I** with aldehydes **II** in basic polar solvents occurs at a higher rate and is characterized by a greater conversion is likely to result from ionization of thiazines **I**.

In order to understand pathways of further transformation of carbinols **V** into chromenecarboxamides **III** we calculated the enthalpies of formation of the initial, intermediate, and final compounds (Table 8, 9) and the energies of transition states at the key stages of the process (Scheme 3). Transition states were identified by searching for such mutual arrangement of the reacting molecules, for which the corresponding reaction centers would be maximally close to each other. The transition state thus determined was assumed to be valid if its calculated vibrational spectrum contained an absorption band with a clearly negative frequency which would correspond to vibration of the reacting centers along the axis passing through these centers.

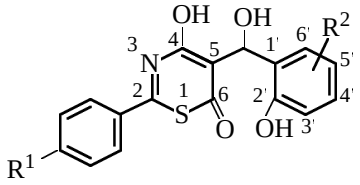
According to the calculations, the formation of carbinol **Vc** from unsubstituted 2-phenylthiazine **Ic** and salicylaldehyde (**IIe**) involves four-center transition state **A** where the C^5–H bond the thiazine and the C=O bond of the aldehyde are coplanar and strictly parallel. This state ensures carbon–carbon bonding between the thiazine C^5 atom and carbonyl carbon atom of the aldehyde, which is accompanied by hydrogen migration from C^5 to the carbonyl oxygen atom. The formation of transition state **A** from unsubstituted thiazine **Ic** requires an energy of activation of 60.5 kcal mol^{-1}; and the heat effect at that stage is –9.6 kcal mol^{-1}. The energy of activation for the formation of analogous transition state (with the same geometric parameters) from the anion of thiazine **Ic** is 40.9 kcal mol^{-1}, and the heat effect increases to –21.1 kcal mol^{-1}.

Table 7. LUMO energies and charges (*q*) and orbital coefficients (*c*) of the carbonyl carbon atoms of substituted salicylaldehydes **IIa**–**IIl**

Comp. no.	R	$-E_{LUMO}$, eV	*q*	*c*
IIa	3-MeO	0.68	0.36	–0.43
IIb	4-Me_2N	0.32	0.37	0.42
IIc	4-MeO	0.57	0.36	–0.42
IId	4-HO	0.61	0.36	0.41
IIe	H	0.66	0.36	0.42
IIf	4-Cl	0.88	0.36	0.39
IIg	4-O_2N	1.77	0.35	0.29
IIh	5-Me_2N	0.49	0.36	0.43
IIi	5-MeO	0.70	0.36	–0.41
IIj	5-HO	0.75	0.36	–0.41
IIk	5-Cl	0.84	0.36	–0.41
IIl	5-O_2N	1.37	0.36	–0.30

Further transformation of carbinols **V** may follow three paths (Scheme 3). The first of these (*a*) includes transformation of **V** into tricyclic intermediate **VI** via attack by the phenolic hydroxy group on the thiazine C^6 atom. The subsequent prototropic rearrangement of intermediate **VI** and cleavage of the C–S bond lead to *N*-(arylcarbothioyl)-2-oxochromene-3-carboxamide **III**. An alternative path of formation of **III** is dehydration of **V** to 5-(arylmethylidene)thiazine **VIII** (Scheme 3, path *b*), followed by intramolecular attack be the phenolic hydroxy group on the thiazine C^6 atom and prototropic rearrangement. The third path (*c*) implies transformation of carbinol **V** into aryl(dithiazinyl)methane **IX** via reaction with the second thiazine molecule; this path is unlikely to occur. In fact, unlike 4,6-dihydroxypyrimidines [5], no aryl(dithiazinyl)methanes **IX** were isolated in the reactions of thiazines **I** with salicylaldehydes. According to the TLC data, in all cases the reaction mixtures contained no other products than chromenecarboxamides **III** and

Table 8. HOMO and LUMO energies, charges on atoms (*q*), and orbital coefficients (*c*) of aryl(thiazinyl)methanols **Va**–**Vf**



Comp. no.	R^1	R^2	$-E_f$, kcal mol^{-1}	*q*				$-E$, eV	
				C^6	C^6=O	$C^{2'}O$	$C^{2'}OH$	HOMO	LUMO
Va	H	H	69.5	0.30	–0.28	–0.25	0.21	9.54	1.27
Vb	H	3-MeO	105.8	0.31	–0.31	–0.24	0.22	9.16	1.34
Vc	H	4-HO	114.5	0.30	–0.28	–0.25	0.22	9.29	1.35
Vd	MeO	H	107.8	0.30	–0.28	–0.25	0.21	9.08	1.34
Ve	MeO	4-HO	152.9	0.31	–0.28	–0.21	0.20	9.15	1.51
Vf	MeO	5-O2N	116.2	0.30	–0.23	–0.24	0.22	9.14	1.44

Comp. no.	*c*							
	C^6		C^6=O		$C^{2'}O$		$C^{2'}OH$	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
Va	0.02	–0.09	0.16	0.08	0.04	0.00	0.00	0.01
Vb	0.01	–0.18	–0.05	0.15	0.16	0.00	0.01	0.01
Vc	–0.03	–0.15	0.11	0.13	0.13	0.00	0.01	0.00
Vd	0.05	–0.16	–0.18	0.14	0.00	0.00	0.01	0.00
Ve	0.00	–0.17	0.02	0.15	0.00	0.00	0.00	0.00
Vf	0.00	–0.01	–0.02	0.02	–0.01	0.04	0.00	0.00

Table 9. Enthalpies of formation (kcal mol^{-1}) of the initial compounds, intermediates, and final products and transition state energies for the reaction of 2-phenyl-4-hydroxy-6*H*-1,3-thiazin-6-one (**Ic**) with salicylaldehyde (**IIe**, R^1 = R^2 = H)

Comp. no.	Neutral molecule	Anion	Comp. no.	Neutral molecule	Anion
I	–7.2	–59.0	**IX**	–15.7	–
II	–52.7	–	A	0.6	–70.8
III	–4.9	92.9	B	–10.3	–
V	–69.5	–132.8	C	–11.1	–127.5
VI	–67.0	–96.3	D	–14.6	–
VII	–0.2	–	E	–33.7	–
VIII	1.8	–47.9	F	47.9	–40.2

benzenecarbothioamides, the latter arising from decomposition of the thiazine ring. In keeping with the calculated data, the process involving formation of aryl(dithiazinyl)methanes **IX** is endothermic [$\Delta_f H^0(0)$ = 7.5 kcal mol^{-1}], and the energy of activation necessary for the formation of transition state **B** is 66.4 kcal mol^{-1}, i.e., it is much greater than the energies of activation along paths *a* and *b* (Table 9).

In order to determine which path, *a* or *b*, is preferred for the transformation of intermediate carbinol **V** into final product **III**, we compared the corresponding energy parameters. According to path a, 2-oxochromene-3-carboxamides **III** are formed via protonation of the C^6=O carbonyl oxygen atom by proton of the phenolic hydroxy group and spontaneous cyclization of the emerging dipolar intermediate (transition state **C**) to chromenothiazine **VI**. The energy of activation for the formation of transition state **C** is 58.4 kcal mol^{-1}, and the heat effect of that stage is 2.5 kcal mol^{-1}. When the anion formed by proton abstraction from the phenolic hydroxy group is involved, the energy of activation decreases to 5.3 kcal mol^{-1}, and the heat effect is –13.4 kcal mol^{-1}. Chromenothiazine **VI** then undergoes dehydration to tricyclic compound **VII** (through transition state **D**,

energy of activation 52.4 kcal mol^{-1}, heat effect 13.3 kcal mol^{-1}), and rearrangement of **VII** yields chromenecarboxamide **III**. The overall heat effect at these stages is 15.8 kcal mol^{-1}.

Path *b* includes dehydration of carbinol **V** to 5-arylmethylidenethiazine **VIII** through transition state **E** (energy of activation 35.8 kcal mol^{-1}, heat effect 17.8 kcal mol^{-1}). Transition state **F** corresponding to intramolecular heterocyclization of 5-arylmethylidenethiazine largely resembles that assumed for the cyclization of aryl(thiazinyl)carbinols: protonation of the C^6=O carbonyl oxygen atom with the phenolic hydroxy proton gives an intermediate which then undergoes rearrangement into structure **VII**. The geometric parameters of the thiazine ring in transition state **F** differ from those typical of transition state **C** due to different electronic structure. The energy of activation for the formation of transition state **F** is 46.1 kcal mol^{-1}, and the heat effect is –2.0 kcal mol^{-1}. The overall heat effect of the above stages is 15.8 kcal mol^{-1}. When the calculations were performed for the process involving the anion formed by deprotonation of the phenolic hydroxy group, the energy of activation was much lower (7.7 kcal mol^{-1}), and the heat effect was much grater (–44.9 kcal mol^{-1}).

We can conclude that the rate-determining stage in the multistep reaction of 2-aryl-4-hydroxy-6*H*-1,3-thiazin6-ones **I** with salicylaldehydes **II** is the formation of aryl(thiazinyl)methanols **V**; this stage is characterized by the highest energy of activation (60.5 kcal mol^{-1} for neutral thiazine **I** and 40.9 kcal mol^{-1} for the corresponding anion). Presumably, the transformation of carbinols **V** into 2-oxochromene-3-carboxamides **III** involves dehydration of the former to 5-arylmethylidenethiazine **VIII**, its subsequent intramolecular cyclization, and cleavage of the C–S bond (path *b*); the energies of activation for both stages along path *b* are lower than the corresponding energies of activation along path *a* (35.8 and 46.1 kcal mol^{-1} against 58.4 and 52.4 kcal mol^{-1}, respectively).

Thus the reaction of 2-aryl-4-hydroxy-6*H*-1,3-thiazin-6-ones with substituted salicylaldehydes can be regarded as a convenient method of synthesis of *N*-(arylcarbothioyl)-2-oxochromene-3-carboxamides.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in DMSO-d6 on a Bruker AM-500 spectrometer (500.17 and 125 MHz, respectively). The IR spectra were measured in KBr on a Specord IR-75 instrument. The electronic absorption spectra were obtained from solutions in ethanol on an SF-2000 spectrophotometer. The mass spectra (electron impact, 70 eV) were run on an MKh-1321 mass spectrometer. The progress of reactions was monitored by TLC on Sorbfil plates (detection under UV light). The yields, melting points, Rf values, and elemental analyses of compounds **IIIa**–**IIIf** are given in Table 1.

***N*-Arylcarbothioyl-2-oxochromene-3-carboxamides IIIa–IIIf** *(general procedure). a*. 2-Hydroxybenzaldehyde **IIa**–**IId**, 4.88 mmol, was added to a solution of 4.88 mmol of 2-aryl-4-hydroxy-6*H*-1,3-thiazin-6-one **Ib** or **Ic** in 10 ml of pyridine. The mixture was thoroughly stirred and heated for 5–10 min at 135–140°C. The mixture was then cooled to 20°C and ground with 25 ml of acetone, and the precipitate was filtered off, washed with 25 ml of acetone, and recrystallized from ethyl acetate. Yield 60–65%.

b. 2-Hydroxybenzaldehyde **IIa**–**IId**, 4.88 mmol, was added to a solution of 4.88 mmol of 2-aryl-4-hydroxy-6*H*- 1,3-thiazin-6-one **Ib** or **Ic** in 5 ml of pyridine, and the mixture was kept for 24 h at 20°C. The precipitate was filtered off and washed with 30 ml of glacial acetic acid and 30 ml of propan-2-ol. No additional recrystallization was necessary. Yield 75–80%.

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