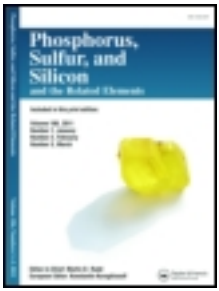

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Chemoselective Pathway to 3-Heteroaryliminomethyl-4-Oxo-4H-Chromenes: Reaction of 4-Oxo-4H-chromene- 3-carboxaldehyde Thiosemicarbazones with Electrophiles in Basic Media

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Chemoselective Pathway to 3-Heteroaryliminomethyl-4-Oxo-4*H*-Chromenes: Reaction of 4-Oxo-4*H*-chromene-3-carboxaldehyde Thiosemicarbazones with Electrophiles in Basic Media

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*The imidazole **4–6** and pyrimidine derivatives **8–11** containing chromone moiety have been obtained through reactions of thiosemicarbazones **1a-c** with some electrophiles in basic media. Compound **12** was also used as a precursor for preparation of some novel 1-[(4-oxo-4H-chromen-3-ylmethylene)amino] [1,3,5]triazine derivatives **13–16**. The formulations of all new products were verified based on their elemental and spectral analysis.*

Keywords Basic media; chromone; electrophiles; thiosemicarbazones

INTRODUCTION

It is known that chromones (4*H*-chromen-4-ones) are widespread in the plant kingdom in a variety of forms and the parent compounds of important flower and fruit pigments.[1] Many natural and synthetic chromone derivatives have unique biological and pharmacological activities, including antiviral,[2,3] antiallergic,[4,5] antimicrobial,[6–9] and neuroleptic activity.[10] Reactivity of chromones towards nucleophiles provides a useful route in the preparation of variety of new heterocyclic systems. Thus, we report here, synthesis of some new nitrogen heterocyclic systems containing chromone moiety through reaction of thiosemicarbazones **1a-c** with some electrophiles under basic media. Thiosemicarbazones **1a-c** have two nucleophilic centers, the first is (NH_2) amino group and the second one is (—NH—C=S) thioimide group. The amino group reacted with the electrophilic reagent first, followed by nitrogen atom not sulfur in thioimide, although the sulfur atom more

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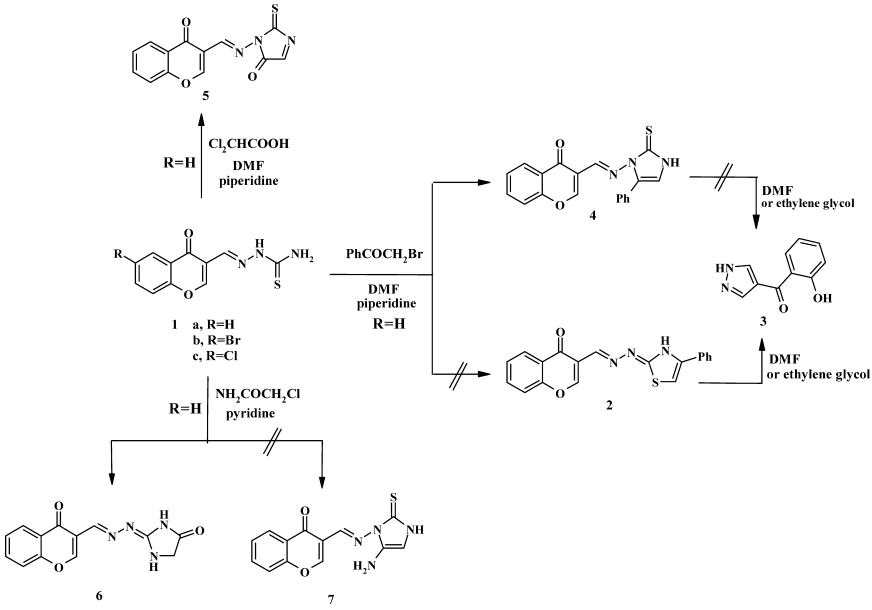


SCHEME 1

nucleophilicity than nitrogen atom. This can be explained on the basis of attack by the anion of –**N**–C=S on electrophile, which is strong nucleophile rather than by the sulfur atom in basic medium (pyridine or DMF).[11,12]

RESULTS AND DISCUSSION

Coutinho and Fernandes[13] obtained the thiazole derivative **2** by reaction of thiosemicarbazone **1a** with phenacyl bromide in DMSO, which underwent ring transformation by boiling in DMF or ethylene glycol to yield 4-(2-hydroxybenzoyl)-1*H*-pyrazole (**3**) (Scheme 1). However, upon carry out reaction **1a** with phenacyl bromide in boiling DMF and drops of piperidine afforded the imidazole derivative **4** and not **2**. Also, boiling **4** in DMF or ethylene glycol, no product could be isolated except **4**, which support its structure (Scheme 1). Compound **4** was confirmed by careful analysis of its spectral data. IR spectrum showed bands of NH, C=O, C=N and C=S at 3118, 1621, 1587, and 1221 cm^{-1}, respectively. ^1H NMR spectrum showed further light on **4** as it showed broad signal at δ 11.54 ppm consistent with for NH of imidazole ring and multiplet signals attributable to aromatic protons at 7.03–7.88 ppm. Moreover, its

mass spectrum showed the molecular ion peak at m/z 347 (M^+, 15.27%) (Table I).

When compound **1a** was allowed to react with dichloroacetic acid in boiling DMF containing few drops of piperidine, 3-[(4-oxo-4*H*-chromen-3-ylmethylene)amino]-2-thioxo-2,3-dihydroimidazol-4-one (**5**) (Scheme 1) was formed and identified by IR spectrum which showed absorption bands at 1624, 1676, and 1283 cm^{-1} corresponding to C=Opyrone, C=Oimidazole and C=S, respectively. Also, its ^1H NMR spectrum showed multiplet signals for C_5—H of imidazole and H—2 of chromone moieties at δ 8.09–8.11 ppm, while its mass spectrum showed the molecular ion peak at m/z 285 (M^+, 25.03%) (Table I).

Unexpectedly, upon reaction thiosemicarbazone **1a** with chloroacetamide in boiling pyridine, 2-[(4-oxo-4*H*-chromen-3-ylmethylene) hydrzino]imidazolidin-4-one (**6**) was smoothly obtained, rather than the expected product of type **7** (Scheme 1). The formula of imidazolidinone **6** was deduced from elemental analysis and spectral data. Thus, its IR spectrum showed disappearance of C=S group and appearance of stretching vibration bands for NH and C=O imidazolinone around 3208 and 1722 cm^{-1}, respectively. Also, its ^1H NMR spectrum revealed the characteristic signals at δ 3.8 and 9.21, 10.37 ppm or CH_2 and NH, NH protons, respectively of imidazolidinone ring. (Table I). The suggested mechanism for formation of compound **6** is removing HCl molecule by reaction **1a** and cholroacetamide to give the intermediate **A** then nucleophilic attack of amino group at thione group C=S to give intermediate **B** followed by elimination of H_2S molecule (Scheme 2).

The present work was extended to investigate the interaction of thiosemicarbazone **1b** with ethyl cyanoacetate in boiling DMF in the presence of piperidine to afford the pyrimidinone derivative **8** (Scheme 3). IR spectrum of **8** revealed NH, C=O pyrimidinone and C=S groups in the region 3433–3268, 1697, and 1234 cm^{-1}, respectively. Its ^1H NMR spectrum revealed the expected characteristic signals CH_2 and NH, NH protons at δ 3.88 and 9.55, 10.08 ppm, respectively. Moreover, mass spectrum of **8** showed a molecular ion peak at m/z 393 (M^+, 1.93%) (Table I).

Also, reaction of **1a** with malononitrile in boiling DMF containing piperidine as catalyst afforded 1-[(4-oxo-4*H*-chromen-3-ylmethylene)amino]-4,6-diamino-2-thioxo-2*H*-pyrimidine (**9**) in good yield (Scheme 3). Formula of **9** was elucidated from elemental analysis and spectral data. Thus, IR spectrum of **9** showed two strong bands at 3413, 3137 (NH_2, NH) and one strong at 1246 cm^{-1} (C=S), while its ^1H NMR spectrum showed two characteristic signals at δ 3.85 and 4.09–4.12 ppm that have been assigned to NH_2, NH_2 protons (Table I).

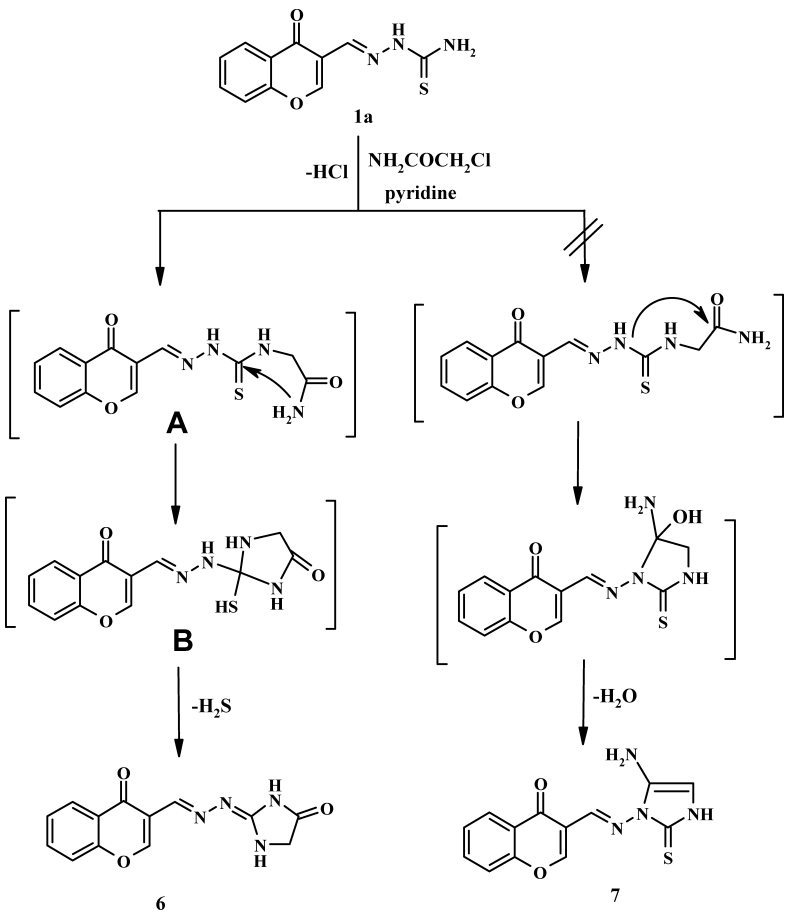
TABLE I The Spectral Data of the New Compounds 4–16

Compd. no.	IR (cm^{-1}) KBr	^{1}H-NMR (DMSO, δ)	MS (m/z,%)
4	3118 (NH), 1621 ($C{=}O_{pyrone}$), 1587 ($C{=}N$), 1221 ($C{=}S$)	7.03–7.09 (m, 9H, Ar—H, H-7, H-8, H-6 and H-5), 7.81–7.88 (m, 3H, H-9, C_4—$H_{imidazole}$and H-2), 11.54 (br, 1H, NH)	348 (M + 1, 0.24), 347 (M^+, 15.27), 300 (6.64), 202 (26.82), 159 (47.56), 120 (100), 92 (66.33), 65 (25.25)
5	1676 ($C{=}O_{imidazolinone}$), 1624 ($C{=}O_{pyrone}$), 1283 ($C{=}S$)	7.07–7.20 (m, 2H, H-7 and H-8), 7.23 (t, 1H, J = 7.5 Hz, H-6), 7.52–7.55 (m, 2H, H-9 and H-5), 8.09–8.11 (m, 2H, C_5—$H_{imidazole}$ and H-2)	289 (M + 4, 0.24), 288 (M + 3, 2.14), 287 (M + 2, 16.47), 286 (M + 1, 82.62), 285 (M^+, 25.03), 241 (13.54), 193 (8.74), 166 (100), 121 (57.47), 94 (43.38), 65 (33.84)
6	3208 (br, NH), 1722 ($C{=}O_{imidazolinone}$), 1620 ($C{=}O_{pyrone}$), 1605 ($C{=}N$)	3.80 (d, 2H, J = 8.4 Hz, CH_2), 7.05–7.08 (m, 4H, H-7, H-8, H-6 and H-5), 7.81–7.84 (m, 2H, H-9 and H-2), 9.21 (s, 1H, NH), 10.37 (s, 1H, NH)	
8	3433, 3268 (NH, NH), 1697 ($C{=}O_{pyrimidinone}$), 1623 ($C{=}O_{pyrone}$), 1596 ($C{=}N$), 1234 ($C{=}S$)	3.88 (s, 2H, CH_2), 7.15–7.18 (m, 2H, H-7 and H-8), 7.50–7.54 (dd, 2H, J = 5.4, 4.8 Hz, H-5), 8.03–8.06 (d, 1H, J = 9.6 Hz, H-9), 8.17–8.22 (d, 1H, J = 9 Hz, H-2), 9.55 (d, 1H, J = 4.2 Hz, NH), 10.08 (s, 1H, NH)	393 (M^+, 1.93), 355 (6.81), 313 (13.80), 199 (5.38), 188 (18.59), 178 (59.50), 178 (59.50), 120 (100), 111 (23.39), 69 (58.56)
9	3413, 3137 (NH_2), 1623 ($C{=}O_{pyrone}$), 1589 ($C{=}N$), 1246 ($C{=}S$)	3.85 (s, 2H, NH_2), 4.09–4.12 (m, 2H, NH_2), 7.09–7.12 (m, 4H, H-7, H-8, H-6 and H-5), 7.95–7.98 (m, 3H, C_5—$H_{pyrimidine}$, H-9 and H-2)	373 (M + $(CH_3)_2CHOH$, 3.63), 372 (7.5), 313 (12.08), 256 (10.5), 239 (65.43), 185 (16.73), 129 (55.64), 121 (32.20), 83 (79.64), 56 (100)

(Continued on next page)

TABLE I The Spectral Data of the New Compounds 4–16 (*Continued*)

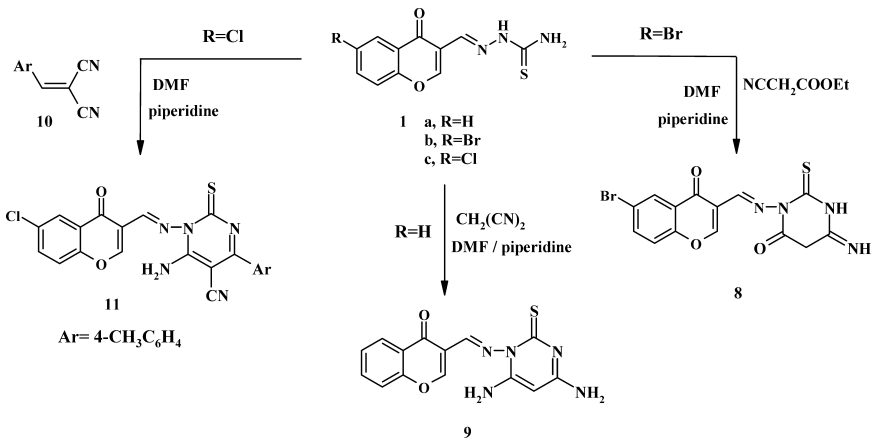
Compd. no.	IR (cm^{-1}) KBr	^{1}H-NMR (DMSO, δ)	MS (m/z,%)
11	3422, 3217 (NH_2), 2216 (C≡N), 1623 ($C{=}O_{pyrone}$), 1589 (C═N), 1241 (C═S)	2.48 (s, 3H, CH_3), 3.85 (s, 2H, NH_2), 7.08–7.13 (m, 7H, Ar—H H-7, H-8 and H-5), 7.97 (br, 1H, H-9), 8.01 (s, 1H, H-2)	451 (M + 3, 10.46), 369 (27.81), 340 (23.21), 271 (33.42), 213 (51.28), 156 (41.84), 155 (5.10), 131 (75.51), 76 (100)
12	3250, 3121 (NH_2, NH), 1621 ($C{=}O_{pyrone}$), 1590 (C═N), 1220, 1153 (2C═S)	7.07–7.25 (m, 3H, H-7, H-8 and H-6), 7.43–7.45 (d, 1H, J = 6 Hz, H-5), 7.92–7.97 (d, 1H, J = 15 Hz, H-9), 8.43 (s, 1H, H-2), 11.39 (br, 2H, NH_2), 11.72 (s, 1H, NH), 12.20 (br, 1H, NH)	
13	3183 (br, OH, NH), 1617 ($C{=}O_{pyrone}$), 1560 (C═N), 1242, 1156 (2C═S)	7.07–7.11 (m, 4H, H-7, H-8, H-6 and H-5), 7.94–7.97 (m, 2H, H-9 and H-2), 10.37 (s, 1H, NH), 11.12 (br, 1H, OH)	
14	3180 (br, NH, NH), 1616 ($C{=}O_{pyrone}$), 1562 (C═N), 1243, 1216, 1156 (3 C═S)	7.05–7.5608 (m, 4H, H-7, H-8, H-6 and H-5), 7.86–7.88 (m, 2H, H-9 and H-2), 10.01 (br, 2H, NH, NH)	346 (M^+, 8.63), 322 (12.26), 305 (30.16), 272 (2.93), 213 (5.67), 178 (100), 159 (19.95), 120 (78.97), 92 (58.13), 65 (27.03)
15	3365 (NH), 1611 ($C{=}O_{pyrone}$), 1595 (C═N), 1219, 1156 (2 C═S)	7.03–7.09 (m, 9H, Ar-H, H-7, H-8, H-6 and H-5), 7.82–7.88 (m, 2H, H-9 and H-2), 11.54 (s, 1H, NH)	392 (M^+, 2.31), 315 (7.72), 269 (4.41), 253 (20.09), 203 (18.01), 178 (76.34), 121 (100), 92 (54.99), 76 (48.08)
16	3197 (br, OH, NH), 1737 ($C{=}O_{carboxylic}$), 1617 ($C{=}O_{pyrone}$), 1568 (C═N), 1244, 1156 (2C═S)	7.08–7.12 (m, 4H, H-7, H-8, H-6 and H-5), 7.94–7.98 (m, 2H, H-9 and H-2), 9.56 (s, 1H, NH), 12.20 (br, 1H, OH)	365 (M + 5, 6.02), 364 (M + 4, 19.33), 363 (M + 3, 6.35), 279 (13.70), 227 (7.10), 202 (12.05), 167 (100), 120 (28.44), 92 (20.78), 77 (14.32)



SCHEME 2

Furthermore, the 6-amino-2-thioxo-1,2-dihydropyrimidine-5-carbonitrile derivative **11** was prepared by reaction of **1c** with arylidenemalononitrile **10** in boiling DMF containing few drops of piperidine (Scheme 3). The IR spectrum of **11** showed vibrations bands at 3422, 3217 cm^{-1} (NH_2) and 2216 cm^{-1} (CN). The ^1H NMR spectrum showed signal at δ 3.85 (NH_2) and multiplet signals at δ 7.08–8.01 ppm for aromatic ring, H-9 and H-2 of chromone moiety. Also, its mass spectrum revealed at m/z 451 (M + 3, 10.46%) corresponding the suggested structure (Table I).

Reaction of **1a** with potassium thiocyanate in refluxing dimethylsulfoxide with a few drops of concentrated hydrochloric acid, gave 1-{[(4-oxo-4*H*-chromen-3-ylmethylene) hydrazino]carbonthioyl}thiourea

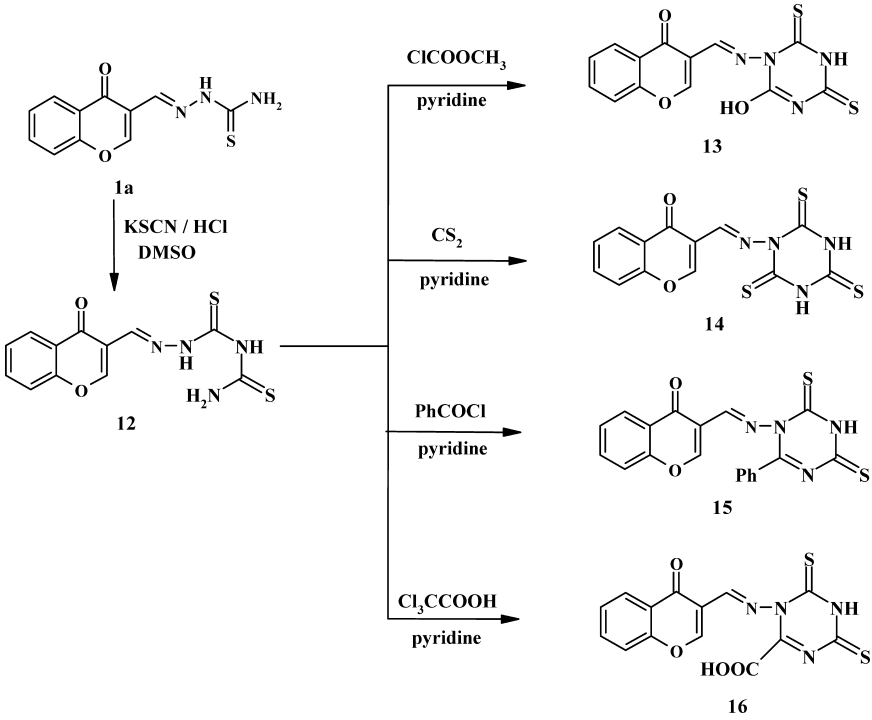


SCHEME 3

(**12**) (Scheme 4). The structure of **12** was rigidly established by studying its spectroscopic properties. Thus, IR spectrum showed strong bands in the regions of 3250 -3121 (NH_2, NH) and 1220–1153 cm^{-1} (C=S). Also, its ^1H NMR spectrum revealed characteristic signals at δ 11.39 and 11.72, 12.20 ppm for NH_2 and NH, NH, respectively (Table I).

Compound **12** was used as a precursor for preparation of 1-[(4-oxo-*4H*-chromen-3-ylmethylene)amino][1,3,5]triazine derivatives **13–16**. Thus, cyclocondensation of **12** with methyl chloroformate and /or carbon disulfide in boiling pyridine gave the 1,3,5-triazine derivatives **13** and **14**, respectively (Scheme 4). Structures of **13** and **14** were established based on their elemental analysis and spectral data. The IR spectra showed the presence of broad band at 3183 cm^{-1} for OH in compound **13**, while showed characteristic band at 1243 cm^{-1} for C=S in compound **14**. ^1H NMR spectrum of **13** exhibited characteristic signals at δ 10.37 and 11.12 ppm for NH and OH protons, respectively, while compound **14** exhibited a broad signal at δ 10.01 ppm for NH protons besides the expected signals of chromone ring (Table I).

Finally, 6-phenyl-2,4-dithioxo-3,4-dihydro[1,3,5]triazine **15** and 4,6-dithioxo-1,4,5,6-tetrahydro[1,3,5]triazine-2-carboxylic acid **16** derivatives have been obtained from reaction of **12** with benzoyl chloride and/or trichloroacetic acid in boiling pyridine, respectively (Scheme 4). The IR spectra of compounds **15** and **16** showed bands at regions 3197–3365 cm^{-1} for NH, OH groups and 1617–1611 cm^{-1} for C=O of chromone moieties. A good evidence for the assigned structures was given from their ^1H NMR spectra as they showed signals at δ 11.54 ppm (NH triazine) in compound **15** and two characteristic signals at δ 9.56 and 12.20 ppm corresponding to (NH triazine) and OH, respectively in compound



SCHEME 4

16. Moreover, their mass spectra revealed at m/z 342 (M^+, 2.31%) and 365 (M + 3, 6.35%) corresponding the expected formulas of **15** and **16**, respectively (Table I).

EXPERIMENTAL

Melting points were determined on a digital Stuart SMP-3 apparatus. Infrared spectra were measured on Perkin-Elmer 293 spectrophotometer (cm^{-1}), using KBr disks. ^1H NMR spectra were measured on Gemini-200 spectrometer (200 MHz), using DMSO-d_6 as a solvent and TMS (δ) as the internal standard. The mass spectra were measured on a HP–MS 5988 mass spectrometer *via* a direct inlet operating at 70 eV. Elemental microanalyses were performed at the microanalysis center at Bulgarian Academy of Science, Sofia, Bulgaria. The physical and spectral data of the new compounds are listed in Tables I and II. 6-Substituted-4-oxo-4*H*-chromene-3-carboxaldehyde thiosemicarbazones (**1a-c**)[14] were prepared by published methods in literature.

TABLE II The Physical and Analytical Data of The New Compounds 4–16

Compd. No.	M.p. °C (yield%)	Solvent of crystallization	Formula (m.wt.)	Calculated/found (%) C	H	N
4	178–180	DMF/EtOH	$C_{19}H_{13}N_3O_2S$	65.69	3.77	12.10
	77%		(347.40)	65.35	3.69	11.93
5	115–117	EtOH	$C_{13}H_7N_3O_3S$	54.73	2.47	14.73
	80%		(285.28)	54.52	2.30	14.51
6	128–130	EtOH	$C_{13}H_{10}N_4O_3$	57.78	3.73	20.73
	49%		(270.25)	57.43	3.61	20.48
8	155–157	MeOH	$C_{14}H_9BrN_4O_3S$	42.76	2.31	14.25
	67%		(393.22)	42.51	2.24	13.98
9	265–267	Isopropanol	$C_{14}H_{11}N_5O_2S$	53.67	3.54	22.35
	78%		(313.34)	53.43	3.38	21.97
11	148–150	EtOH	$C_{22}H_{14}ClN_5O_2S$	59.00	3.15	15.64
	43%		(447.91)	58.62	2.88	15.38
12	116–118	diluted EtOH	$C_{12}H_{10}N_4O_2S_2$	47.05	3.29	18.29
	90%		(306.37)	46.71	3.15	17.90
13	206–208	EtOH	$C_{13}H_8N_4O_3S_2$	46.98	2.43	16.86
	77%		(332.36)	46.72	2.33	16.59
14	188–190	DMF/EtOH	$C_{13}H_8N_4O_2S_3$	44.81	2.31	16.08
	59%		(348.43)	44.53	2.17	15.81
15	260–262	EtOH	$C_{19}H_{12}N_4O_2S_2$	58.15	3.08	14.28
	85%		(392.46)	57.83	2.92	13.99
16	204–206	DMF/EtOH	$C_{14}H_8N_4O_4S_2$	46.66	2.24	15.55
	71%		(360.37)	46.34	2.09	15.29

1-[(4-Oxo-4*H*-chromen-3-ylmethylene)amino]-5-phenyl-2-thioxo-2,3-dihydro-imidazole (4)

A mixture of compound **1a** (2.47 g, 10 mmol) and phenacyl bromide (1.99 g, 10 mmol) in dimethylformamide (50 ml) containing two drops of piperidine, was refluxed for 8 h. The solution was cooled and poured onto ice—water. The solid obtained was filtered off and crystallized from the proper solvent to give **4** (Table II).

3-[(4-Oxo-4*H*-chromen-3-ylmethylene)amino]-2-thioxo-2,3-dihydroimidazol-4-one (5)

A mixture of compound **1a** (2.47 g, 10 mmol) and dichloroacetic acid (1.40 g, 10 mmol) in dimethylformamide (50 ml) containing two drops of piperidine, was refluxed for 8 h. The solution was cooled and poured onto ice—water. The solid obtained was filtered off and crystallized from the proper solvent to give **5** (Table II).

2-[(4-Oxo-4*H*-chromen-3-ylmethylene)hydrazino]imidazolidin-4-one (6)

A mixture of compound **1a** (2.47 g, 0.01 mol) and chloroacetamide (0.91 g, 0.01 mol) in dry pyridine (50 ml) was refluxed for 10 h. The solution was cooled and poured onto ice—HCl. The solid obtained was filtered off and crystallized from the proper solvent to give **6** (Table II).

6-Imino-3-[(6-bromo-4-oxo-4*H*-chromen-3-ylmethylene)amino]-2-thioxo-tetrahydropyrimidin-4-one (8)

A mixture of compound **1b** (3.26 g, 10 mmol) and ethyl cyanoacetate (1.11 g, 10 mmol) in dimethylformamide (50 ml) containing two drops of piperidine was refluxed for 12 h. The solution was cooled and poured onto ice—water. The solid obtained was filtered off and crystallized from the proper solvent to give **8** (Table II).

1-[(4-Oxo-4*H*-chromen-3-ylmethylene)amino]-4,6-diamino-2-thioxo-2H-pyrimidine (9)

A mixture of compound **1a** (2.47 g, 10 mmol) and malononitrile (0.66 g, 10 mmol) in dimethylformamide (50 ml) containing two drops of piperidine was refluxed for 8 h. The solution was cooled and poured onto ice—water. The solid obtained was filtered off and crystallized from the proper solvent to give **9** (Table II).

6-Amino-4-(4-methylphenyl)-1-[(6-chloro-4-oxo-4*H*-chromen-3-ylmethylene) amino]-2-thioxo-1,2-dihydropyrimidine-5-carbonitrile (11)

A mixture of compound **1c** (2.81 g, 10 mmol) and arylidenemalononitrile **10** (1.68 g, 10 mmol) in dimethylformamide (50 ml) containing two drops of piperidine was refluxed for 10 h. The solution was cooled and poured onto ice—water. The solid obtained was filtered off and crystallized from the proper solvent to give **11** (Table II).

1-{[(4-Oxo-4*H*-chromen-3-ylmethylene)hydrazino] carbonthioyl}thiourea (12)

A mixture of compound **1a** (2.47 g, 10 mmol) and potassium thiocyanate (0.97 g, 10 mmol) in dimethylsulfoxide (50 ml) in the presence of concentrated hydrochloric acid (0.5 ml) was refluxed for 4 h. The

solution was cooled and poured onto ice—water. The solid obtained was filtered off and crystallized from the proper solvent to give **12** (Table II).

1-[(4-Oxo-4*H*-chromen-3-ylmethylene)amino]-4,6-dithioxo-3,4-dihydro-6-hydroxy-1,3,5-triazine (13)

A mixture of compound **12** (3.06 g, 10 mmol) and methyl chloroformate (0.92 g, 10 mmol) in dry pyridine (50 ml) was refluxed for 6 h. The solution was cooled and poured onto ice—HCl. The solid obtained was filtered off and crystallized from the proper solvent to give **13** (Table II).

1-[(4-Oxo-4*H*-chromen-3-ylmethylene)amino]-2,4,6-trithioxo-1,2-tetrahydro-1,3,5-triazine (14)

A mixture of compound **12** (3.06 g, 10 mmol) and carbon disulfide (1.14 g, 20 mmol) in dry pyridine (50 ml) was refluxed for 10 h. The solution was cooled and poured onto ice—HCl. The solid obtained was filtered off and crystallized from the proper solvent to give **14** (Table II).

1-[(4-Oxo-4*H*-chromen-3-ylmethylene)amino]-6-phenyl-2,4,dithioxo-3,4-tetrahydro-1,3,5-triazine (15)

A mixture of compound **12** (3.06 g, 10 mmol) and benzoyl chloride (1.40 g, 10 mmol) in dry pyridine (50 ml) was refluxed for 6 h. The solution was cooled and poured onto ice—HCl. The solid obtained was filtered off and crystallized from the proper solvent to give **15** (Table II).

1-[(4-Oxo-4*H*-chromen-3-ylmethylene)amino]-4,6-dithioxo-1,4,5,6-tetrahydro-1,3,5-triazine-2-carboxylic acid (16)

A mixture of compound **12** (3.06 g, 10 mmol) and trichloroacetic acid (1.74 g, 10 mmol) in dry pyridine (50 ml) was refluxed for 8 h. The solution was cooled and poured onto ice—HCl. The solid obtained was filtered off and crystallized from the proper solvent to give **16** (Table II).

REFERENCES

[1] G. P. Ellis, Chromenes, chromanones, and chromones. In *The Chemistry of Heterocyclic Compounds* (Wiley, New York, 1977), Vol. 31, pp. 921–940.

[2] M. Yun, C. Shuang, F. Wei, R. C. Lin, P. P. But, H. S. Lee, and S. F. Lee, *Chem. Pharm. Bull.*, **51** (11), 1264 (2003).

[3] N. Desideri, P. Mastromarino, and C. Conti, *Antiviral Chem. Chemother.*, **14** (4), 195 (2003).
[4] J. Bolos, S. Gubert, L. Anglada, J. M. Planas, C. Burgarolas, J. M. Castello, A. Sacristan, and J. A. Ortiz, *J. Med. Chem.*, **39,** 2962 (1996).
[5] S. G. Jagadeesh, D. G. L. Krupadanam, and G. Srimannarayan, *Indian J. Chem.*, **36B,** 965 (1997).
[6] A. A. Deshpande, A. P. Karale, B. K. Bhirud, and S. B. Gill, *Indian J. Chem. Sect. B: Org. Chem. Includ. Med. Chem.*, **44B** (2), 422 (2005).
[7] N. Z. Siddiqui, G. Khuwaja, and M. Asad, *Heterocyclic Commun.*, **12**(6), 443 (2006).
[8] H. Z. Chohan, A. Rauf, M. M. Naseer, A. M. Somra, and T. C. Supuran, *J. Enzyme Inhib. Med. Chem.*, **21** (2), 173 (2006).
[9] T. E. Ali, *Phosphorus, Sulfur and Silicon* **182(8),** 1717 (2007).
[10] V. Y. Sosonvskikh, B. I. Usachev, A. Y .Sizov, and M. I. Kodess, *Tetrahedron Lett.*, **45,** 7351 (2004).
[11] A. S. A. Youssef, *Phosphorus, Sulfur, and Silicon*, **177,** 173 (2002).
[12] K. A. Kandeal, *Ann. Rev.*, **16,** 606 (1991).
[13] D. L. Coutinho and P. S. Fernandes, *Indian J. Chem.*, **31B,** 573 (1992).
[14] H. M. El–Shaaer, S. S. Ibrahim, and A. M. Abdel–Halim, *J. Chem. Soc. Pak.*, **17** (3), 165 (1995).