Reaction of some Coumarin and 4,6-Diaryl-2*H*-pyran Derivatives with Secondary Amines

Ibrahim El-Sayed El-Kholy, Morcos Michael Mishrikey and Hassan Mostafa Feid-Allah

Chemistry Department, Faculty of Science, Alexandria University, Moharram Bey, Alexandria, Egypt

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The reaction of piperidine, morpholine, piperazine or dimethylamine with several coumarins, 3-bromocoumarin, 4,6-diaryl-2*H*-pyran-2-ones and 3-bromo-4,6-diaryl-2*H*-thiopyran-2-ones gave *o*-hydroxycinnamic acid amides, benzofurans, open-chain δ-oxoamides and thiophene derivatives, respectively.

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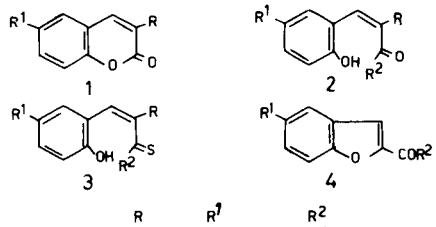
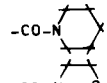
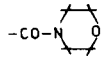
In an earlier publication (1) we reported that the reaction of piperidine or morpholine with 4,5,6-triaryl-2*H*-pyran-2-ones led to the formation of 1,5-dioxo-1-(*N*-piperidino- or morpholino)-3,4,5-triarylpent-3-enes. The isolation of these δ-oxo-amides suggests the fission of the 2-pyrone ring at the 1,2-bond which is commonly accepted, without isolation of intermediates, for the reaction of ammonia or amines with 2*H*-pyran-2-ones. In the present study, the reaction of several secondary amines with other 2*H*-pyran-2-ones and coumarins is described. Moreover, some of the synthesized compounds have piperidinyl or morpholinyl groups in addition to the physiologically active coumarin nucleus, which may be valuable therapeutic agents.

In the reaction of piperidine, morpholine or piperazine with coumarin, 3-acetyl- or 6-nitrocoumarins **1a,d,e**, *o*-hydroxycinnamic acid amides **2a-e** were obtained. Thiocoumarin behaved similarly with piperidine affording the thioamide **3a**. Moreover, while most of the above coumarin derivatives underwent resinification on reaction with dimethylamine, coumarin itself gave *o*-hydroxycinnamic acid *N,N*-dimethylamide (**2f**). It is worthy to mention that the amides **2a-c** were also obtained from the reaction of coumarin 3-carboxylic acid (**1g**) with the respective amine, which suggests decarboxylation to coumarin during reaction with the heterocyclic base. Also, *o*-hydroxycinnamic acid piperidide (**2a**) was reported (2) to be formed from the reaction of piperidine with 3-carboethoxycoumarin.

Coumarin-3-carbonylpiperidine (**1h**) and morpholine (**1i**) were obtained from coumarin-3-carboxylic acid (**1g**) by conversion to the acid chloride and subsequent reaction with piperidine or morpholine. The infrared spectra of the amides **1h,i** exhibited two bands in the ranges 1640 and 1700-1720 cm^{-1} due to tertiary amide and coumarin carbonyl absorptions, respectively. In their ^1H nmr spectra, a separate signal could be assigned for the C-4 proton in the range δ 7.9-8.0. The pronounced deshielding of this proton can be attributed to the electronic effects of the B-carbonyl amide which are probably enhanced by its magnetic anisiotropy. The reaction of the coumarin amide **1h** with piperidine afforded α-carbonylpiperidine *o*-hydroxycinnamic acid piperidide (**2h**).

In agreement with the suggested structures, the infrared spectra of the amides **2** exhibited a tertiary amide carbonyl and OH absorptions at 1640-1645 and 3400-3500 cm^{-1}, respectively, while the thioamide **3a** showed a thiocarbonyl band at 1110 cm^{-1}. It is observed that in their ^1H nmr spectra no separate signals could be assigned for the olefinic H_α, and H_β protons which probably resonate in the aromatic protons region.



	R	R^1	R^2
a	H	H	
b	H	H	
c	H	H	
d	$COCH_3$	H	
e	H	NO_2	
f	H	H	
g	COOH	H	
h		H	
i		H	
j	Br	H	
k	Br	H	
l	Br	H	

The structure of the *o*-hydroxycinnamic acid amides **2** was further confirmed from their mass spectral data.

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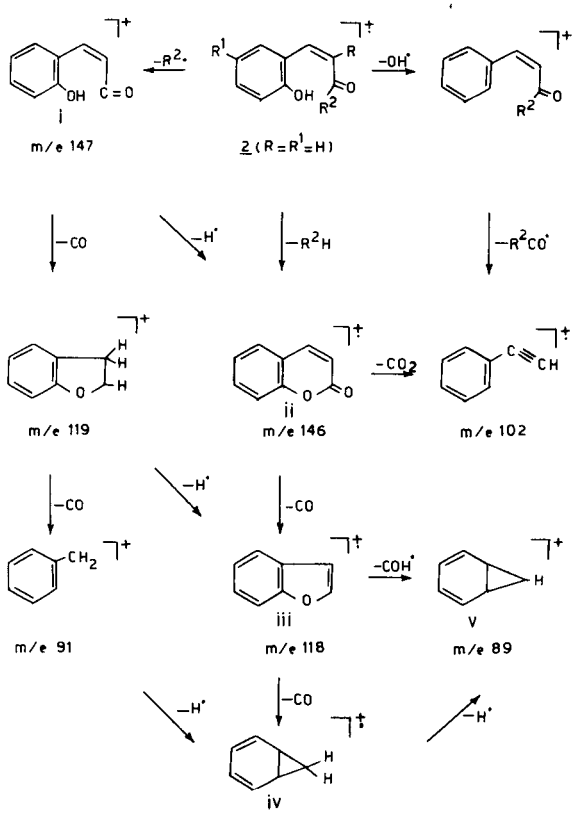


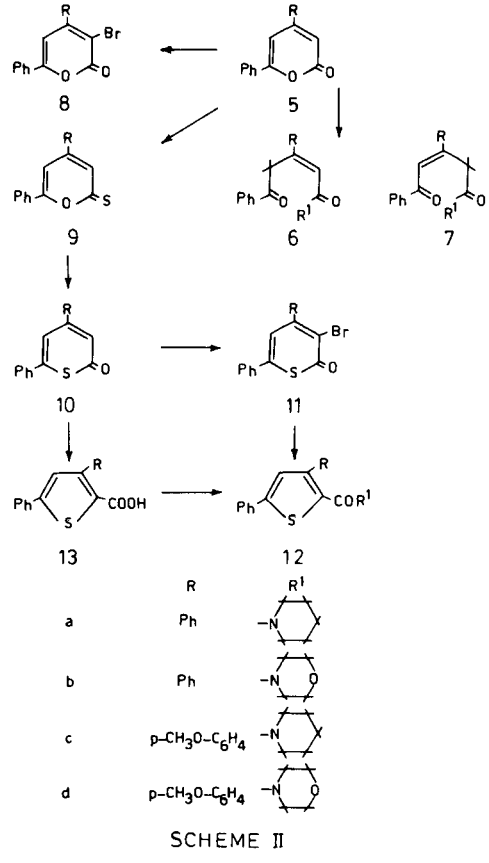
SCHEME I

These compounds gave moderately intense molecular ion peaks and the common prominent peaks in their spectra were observed at m/e 147, 146, 119, 118, 102, 91, 90 and 89, which can be assigned to the fragments shown in Scheme I. Loss of amine radical from the molecular ion leads to the intense cation *i* at m/e 147, which in case of **2f** was the base peak, while elimination of a secondary amine molecule gives coumarin species *ii* at m/e 146. The latter subsequently fragments by loss of CO to benzofuran *iii* at m/e 118 which can also be formed from *i* by successive loss of CO and H. Fragmentation of benzofuran gives rise to the species *iv* at m/e 90 by loss of CO or cation *v* at m/e 89 by elimination of CHO radical.

It is worthy to mention that the fragmentation pattern of coumarin-3-carbonylpiperidine (**1h**) was similar to that of the above amides since successive loss of piperidine radical and CO leads to coumarin.

The reaction of 3-bromocoumarin with piperidine was reported (3) to give a mixture including the substitution products 3- and 4-piperidinylcoumarins as well as α,β-dipiperidinyl-*o*-hydroxycinnamic acid piperidide and 3-piperidinyl-2,3-dihydrobenzofuran-2-carboxylic acid piperidide arising by fission of the coumarin ring. However, in the present study, the reaction of 3-bromocoumarin (**1j**) with piperidine, morpholine or piperazine afforded the benzofuran-2-carboxylic acid amides **4a-c**, which are assumed to be formed *via* the open-chain amides **2j-l** and subsequent elimination of hydrogen bromide. The structure of these amides was proved by synthesis from benzofuran-2-carboxylic acid when its acid chloride was treated with the appropriate amine.

The infrared spectra of the above benzofuran-amides showed a tertiary amide carbonyl at 1630-1650 cm^{-1} and their ^1H nmr spectra exhibited the characteristic signals of the amine while no separate resonance could be assigned to the C-3 furan ring proton which is overlapped by the aromatic protons. The prominent peaks in the mass spectrum of benzofuran-2-carboxylic acid piperidide (**4a**) are those due to fragmentation of benzofuran arising by successive loss of amine radical and CO from the molecular ion.



SCHEME II

Similar to 4,5,6-triaryl-2*H*-pyran-2-ones (1), the reaction of 4,6-diphenyl-2*H*-pyran-2-one (**5a**) with piperidine and morpholine gave the open-chain δ-oxo-amides **6a,b** or **7a,b**. The ^1H nmr of spectra of these compounds exhibited a methylene singlet at δ 4.8 and an olefinic proton at δ 6.7 which cannot differentiate between the two possible structures **6** or **7**. However, the α,β-unsaturated amide structure **6** may be more favoured since their infrared spectra showed two bands at 1612 and 1685 cm^{-1} due to α,β-unsaturated tertiary amide and carbonyl absorptions, respectively (Scheme II).

Table I

Analytical Data of Coumarin and Benzofuran Derivatives

Compound No.	M.p. °C	Formula	Calcd. % C	Calcd. % H	Calcd. % N	Found % C	Found % H	Found % N
1h	186	$C_{15}H_{15}NO_3$	70.0	5.9	5.4	69.7	5.6	5.7
1i	120 (a)	$C_{14}H_{13}NO_4$	64.8	5.1	5.4	64.5	5.5	5.6
2a	225 (b)	$C_{14}H_{17}NO_2$	72.7	7.4	6.1	72.5	7.2	6.1
2b	200	$C_{13}H_{15}NO_3$	66.9	6.5	6.0	66.8	6.3	5.8
2c	158	$C_{13}H_{16}N_2O_2$	67.2	6.9	12.1	67.1	6.6	12.1
2d	155	$C_{16}H_{19}NO_3$	70.3	7.0	5.1	70.1	7.3	5.4
2e	249	$C_{14}H_{16}N_2O_4$	60.8	5.8	10.1	60.6	5.8	10.0
2f	218	$C_{11}H_{13}NO_2$	69.1	6.8	7.3	69.3	6.5	7.2
2h	85	$C_{20}H_{26}N_2O_3$	70.1	7.6	8.2	70.2	7.4	8.3
3a	162 (c)	$C_{14}H_{17}NOS$	68.0	6.9	5.7	67.8	6.7	5.5
4a	65	$C_{14}H_{15}NO_2$	73.3	6.6	6.1	73.0	6.6	6.1
4b	95	$C_{13}H_{13}NO_3$	67.5	5.7	6.1	67.6	5.7	6.1
4c	235	$C_{13}H_{14}N_2O_2$	67.8	6.1	12.2	67.5	5.8	12.3

(a) Reference 2, m.p. 169°. (b) Reference 2, m.p. 221°. (c) Calcd. for S: 13.0%. Found: 13.0%.

Table II

Infrared and ^{1}H Nmr Spectral Data of Coumarin and Benzofuran Derivatives

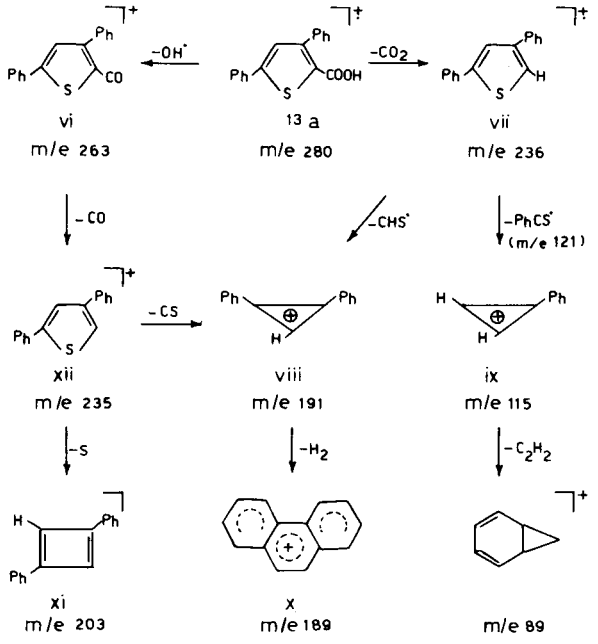
Compound No.	Ir (cm^{-1}) C=O Amide	Ir (cm^{-1}) C=O Coumarin	Ir (cm^{-1}) OH	^{1}H Nmr Chemical Shift (δ/ppm) (a) Piperidine or Morpholine	^{1}H Nmr Chemical Shift (δ/ppm) (a) Ar-H and Olefinic (m)	^{1}H Nmr Chemical Shift (δ/ppm) (a) Others
1h (b)	1640	1720		1.7 (6H), β and γ-protons, 3.2 (2H), α-axial, 3.8 (2H) α-equatorial (c)	7.5 (4H)	7.9 (s,s 1H, H-4)
1i	1640	1700		3.7 (8H)	7.6 (4H)	8.0 (s, 1H, H-4)
2a	1645		3400	1.5 (6H), and β and γ-protons 3.5 (4H), α-protons	7.4 (6H)	9.9 (s, 1H, OH) (d)
2b	1640		3400			
2c (e)	1640		3500			
2d (f)	1630		3400			
2e (b) (g)	1650		3500	1.5 (6H), β and γ-protons, 3.5 (2H) α-axial, 4.3 (2H), α-equatorial	7.7 (5H)	
2f (b)	1640		3500		7.3 (6H)	2.9 (s, 6H, 2N-CH_3)
2h	1640, 1665		3500			
3a	1110 (h)		3400	1.5 (6H), β and γ-protons, 3.8 (2H) α-axial, 4.2 (2H) α-equatorial	7.4 (6H)	
4a	1650			1.7 (6H), β and γ-protons 3.8(4H), α-protons	7.4 (5H)	
4b	1630			3.9 (8H)	7.5 (5H)	
4c (e)	1640					

(a) s: singlet, m: multiplet. (b) ^{1}H Nmr spectra carried out in DMSO-d_6. (c) The low field multiplet can be assigned to the equatorial protons since the axial protons usually resonate at higher fields (7). (d) Exchangeable with deuterium oxide. (e) Piperazine NH absorption at 3250 cm^{-1}. (f) Acetyl C=O at 1660 cm^{-1}. (g) NO_2 absorption at 1350 and 1520 cm^{-1}. (h) C=S absorption.

Bromination of the 2*H*-pyran-2-ones **5a,c** afforded the 3-bromo derivatives **8a,c**. While the ^{1}H nmr spectrum of 4,6-diphenyl-2*H*-pyran-2-one (**5a**) exhibited two doublets (J = 1.5 Hz) at δ 6.4 and δ 6.9 for the two allylic coupled C-5 and C-3 protons, respectively, its 3-bromo derivative **8a** showed a singlet at 6.7 for the C-5 proton. The reaction of the above bromopyrones with piperidine or morpholine afforded resinous products which could not be identified.

4,6-Diaryl-2*H*-pyran-2-thiones **9a,c** could be quantitatively converted into the corresponding 2*H*-thiopyran-2-ones **10a,c** on treatment with aqueous sodium carbonate or piperidine. Such facile transformation which was also reported (1) for 4,5,6-triaryl-2*H*-pyran-2-thiones demonstrates the wide spectrum of the above reaction as a

simple synthetic route for 2*H*-thiopyran-2-ones. While no definite products could be isolated from the reaction of 2*H*-thiopyran-2-ones with piperidine or morpholine, their 3-bromo derivatives **11a,c** gave with these reagents the corresponding 3,5-diarylthiophene-2-carboxylic acid piperidides or morpholides **12a,b,d**. Compounds **12a,b** were also formed from 3,5-diphenylthiophene-2-carboxylic acid (**13a**) by treatment of its acid chloride with the respective amine. The thiophene acid **13a** was obtained by the action of alcoholic potassium hydroxide on the corresponding 2*H*-thiopyran-2-one **10a** (Scheme II).



SCHEME III

The mass spectrum of the thiophene acid **13a** (Scheme III) exhibited the molecular ion as the base peak and the most intense peaks were observed at m/e 263, 236, 235, 203, 191, 189, 121, 115 and 89. Elimination of OH radical from the molecular ion gives rise to the cation *vi* at m/e 263 while loss of CO_2 gives 3,5-diphenylthiophene radical cation *vii* at m/e 236. Subsequent fragmentation of *vii* accounts for the observation of the cyclopropenium cations *viii* at m/e 191 and *ix* at m/e 115 arising by elimination of CHS ad PhCS (m/e 121) radicals, respectively. The species *x* at m/e 189 can be considered to arise by loss of H_2 molecule from *viii* (4), while the cyclobutadiene cation *xi* at m/e 203 may be formed by elimination of S from *xii*, which is usually observed for phenyl substituted thiophenes (5).

It is worthy to mention that 3,5-diphenylthiophene-2-carboxylic acid morpholide (**12b**) and 3-bromo-4,6-diphenyl-2*H*-thiopyran-2-one (**11a**) exhibited similar fragmentation patterns since successive loss of morpholine radical and CO from **12b** or Br and CO from **11a** leads to the cation *xii* (Scheme III).

EXPERIMENTAL

Microanalyses were performed by Microanalysis Unit, Cairo University, Cairo. Infrared spectra were measured with a Unicam SP 1025 spectrophotometer for potassium bromide pellets or in Nujol. The ^{1}H nmr spectra were recorded on a Varian T-60 spectrometer for solutions in deuteriochloroform with TMS as internal standard. Mass spectra were recorded on an LKB 9000 instrument.

o-Hydroxycinnamic Acid Amides (Tables I and II).

A solution of the appropriate coumarin (1 g., 0.005-0.007 mole) in the suitable amine (6 ml.) was refluxed for 5-8 hours. The amides (70% yield) which separated after dilution with water were crystallized from ethanol or ethanol-benzene. Compounds **2a-c** were also obtained (60% yield) when coumarin-3-carboxylic acid (1 g., 0.0052 mole) was refluxed with piperidine or morpholine for six hours; ms: m/e (relative intensity) (compound **2a**) M^+ 231 (11), 230 (4), 214 (4), 148 (7), 147 (59), 146 (7), 138 (5), 120 (7), 119 (4), 118 (14), 104 (4), 103 (36), 102 (2), 91 (26), 90 (5), 89 (5), 86 (7), 85 (77), 84 (100), 83 (5), 65 (8); (compound **2f**) M^+ 191 (30), 174 (3), 148 (10), 147 (100), 146 (7), 120 (3), 119 (5), 118 (24), 104 (8), 103 (90), 102 (2), 101 (5), 92 (5), 91 (46), 90 (8), 89 (10), 77 (6), 72 (20), 65 (16).

o-Hydroxycinnamic Acid Thiopiperidide (**3a**) (Tables I and II).

A solution of thiocoumarin (1 g., 0.006 mole) in piperidine (6 ml.) was refluxed for four hours. The thioamide **3a** (70% yield) which separated after dilution with water was crystallized from ethanol in needles.

Coumarin-3-carbonylpiperidine or Morpholine (Tables I and II).

Coumarin-3-carbonyl chloride (1 g., 0.0048 mole) was heated with piperidine or morpholine (5 ml.) for 10 minutes on a water bath. After removal of the excess amine, the residue was treated with cold methanol and the separated amides (60% yield) were crystallized from methanol in needles; ms: m/e (relative intensity) (compound **1h**) M^+ 257 (26), 256 (3), 174 (4), 173 (27), 147 (10), 146 (15), 145 (3), 118 (5), 102 (7), 101 (11), 90 (2), 89 (9), 85 (8), 84 (100), 82 (8).

α-Carbonylpiperidine-*o*-hydroxycinnamic Acid Piperidide (**2h**) (Tables I and II).

A solution of coumarin-3-carbonylpiperidine (0.5 g., 0.0019 mole) in piperidine (8 ml.) was refluxed for six hours. After removal of excess piperidine, the residue was treated with methanol and the product (55% yield) was crystallized from methanol.

Benzofuran-2-carboxylic Acid Amides (Tables I and II).

3-Bromocoumarin (1 g., 0.0044 mole) was heated with the appropriate amine for 30 minutes on a water bath and then excess amine was removed. The residue afforded the benzofuran amides (65% yield) on treatment with cold methanol which were crystallized from ethanol in needles. The above compounds were also obtained (80% yield) when coumarilyl chloride (0.5 g., 0.0027 mole) was treated with the suitable amine at room temperature; ms: m/e (relative intensity) (compound **4a**) M^+ 229 (68), 228 (9), 200 (6), 174 (5), 173 (4), 161 (4), 160 (6), 147 (6), 146 (23), 145 (100), 144 (3), 131 (5), 119 (4), 118 (23), 90 (6), 89 (38), 84 (30), 83 (8), 69 (6).

1,5-Dioxo-1-(*N*-piperidino or morpholino)-3,5-diphenylpent-2-enes (Tables III and IV).

A solution of 4,6-diphenyl-2*H*-pyran-2-one (0.5 g., 0.002 mole) in piperidine or morpholine (3 ml.) was refluxed for three hours. The amides (70% yield) which separated after dilution with water were crystallized from ethanol; ms: m/e (relative intensity) (compound **6a**) M^+ 333 (18), 250 (3), 249 (21), 248 (68), 229 (7), 228 (46), 221 (17), 220 (67), 192 (14), 191 (33), 190 (4), 189 (7), 165 (4), 145 (7), 115 (23), 106 (7), 105 (92), 85 (26), 84 (100), 77 (48), 69 (8).

3-Bromo-4,6-diaryl-2*H*-pyran-2-ones (Tables III and IV).

A solution of 4,6-diaryl-2*H*-pyran-2-one (1 g., 0.004 mole) in chloroform

Table III

Analytical Data of 4,6-Diaryl-2*H*-pyran-2-one Derivatives

Compound	M.p. °C	Formula	Calcd. % C	H	N	S	Br	Found % C	H	N	S	Br
6a	108	$C_{22}H_{23}NO_2$	79.2	6.9	4.2	4.2		78.9	7.0	3.9		
6b	102	$C_{21}H_{21}NO_3$	75.2	6.3	4.2			75.4	6.6	4.2		
8c	174	$C_{18}H_{13}BrO_3$	60.5	3.7			22.4	60.3	3.9			22.1
11a	173	$C_{17}H_{11}BrOS$	59.5	3.2		9.3	23.3	59.3	3.2		9.6	23.6
11c	135	$C_{18}H_{13}BrO_2S$	57.9	3.5		8.6	21.4	57.8	3.2		8.4	21.6
12a	138	$C_{22}H_{21}NOS$	76.0	6.1	4.0	9.2		76.1	6.3	4.2	9.2	
12b	215	$C_{21}H_{19}NO_2S$	72.2	5.5	4.0	9.2		72.4	5.6	4.3	9.2	
12d	148	$C_{22}H_{21}NO_3S$	69.6	5.6	3.7	8.4		69.5	5.3	3.8	8.4	
13a	235	$C_{17}H_{12}O_2S$	72.8	4.3		11.4		73.0	4.4		11.3	

Table IV

Infrared and ^{1}H Nmr Spectral Data of 4,6-Diaryl-2*H*-pyran-2-one Derivatives

Compound No.	Ir (Cm^{-1}) C=O Amide	C=O 2-Pyrone	^{1}H Nmr Chemical Shift (δ/ppm) (a) Piperidine or Morpholine Protons (m)	H-3	H-5	Ar-H (m)
5a		1702 (b)		6.9 (d)	6.4 (d)	7.7 (10H)
6a (c)	1612	1685 (d)	1.7 (6H), β and γ-protons 3.6 (4H) α-protons	6.7 (s) (e)		7.7 (10H)
6b	1617	1688 (d)				
8a		1715			6.7 (s)	
8b		1725				
11a		1630			7.0 (s)	7.4 (10H)
11c		1645				
12a	1618					
12b	1630		3.3 (8H)			7.4 (11H) (f)
12d	1625					
13a	1635 (g)					

(a) s: Singlet; d: doublet (J = 1.5 Hz); m: multiplet. (b) Taken from reference 6. (c) The ^{1}H nmr spectrum of this compound showed also a CH_2 singlet at δ 4.8. (d) C=O ketonic. (e) This signal is due to the H-2 proton. (f) The H-4 thiophene ring proton is overlapped by the aromatic protons. (g) C=O carboxylic.

(20 ml.) was refluxed with bromine (0.6 g., 0.0075 mole) for four hours. After evaporation of the solvent, treatment of the residue with cold methanol, the bromopyrones which separated in quantitative yield were crystallized from ethanol.

4,6-Diaryl-2*H*-thiopyran-2-ones (Table IV).

A suspension of 4,6-diaryl-2*H*-pyran-2-thione **9a,c** (6) (1 g., 0.0038 mole) in methanol (25 ml.) was refluxed with 10% aqueous sodium carbonate (5 ml.) for one hour. The 2*H*-thiopyran-2-one, which separated in 85% yield after dilution with water, crystallized from methanol in yellow needles. Compounds **10a,c** were also prepared (70% yield) when a suspension of **9a,c** (0.5 g., 0.0019 mole) in methanol (15 ml.) was kept with piperidine (1 ml.) at 20° overnight.

3-Bromo-4,6-diaryl-2*H*-thiopyran-2-ones (Tables III and IV.

A solution of 4,6-diaryl-2*H*-thiopyran-2-one (1 g., 0.0038 mole) in chloroform (15 ml.) was gradually treated with bromine (0.6 g., 0.0075 mole) in chloroform (10 ml.) and refluxed for four hours. After evaporation of the solvent and addition of methanol the bromoderivatives which separated (quantitative yield) were crystallized from ethanol in yellow needles; ms: m/e (relative intensity) (compound **11a**) M^+ 344, 342 (28), 317 (13), 316 (59), 315 (13), 314 (57), 265 (8), 264 (24), 263 (100), 262 (5), 236 (12), 235 (13), 234 (44), 232 (4), 229 (10), 203 (6), 202 (33), 201 (8), 200 (7), 192 (7), 191 (30), 190 (5), 189 (16), 165 (13), 163 (5), 158 (9), 157 (6), 145 (13), 133 (7), 121 (12), 118 (6), 117 (23), 116 (5), 115 (3), 104 (6), 103 (5), 102 (22), 101 (18), 100 (7), 94 (7), 93 (4), 90 (4), 89 (28), 77 (13).

3,5-Diphenylthiophene-2-carboxylic acid (**13a**) (Tables III and IV).

A solution of 3-bromo-4,6-diphenyl-2*H*-thiopyran-2-one (1 g., 0.003 mole) in 5% methanolic potassium hydroxide (20 ml.) was refluxed for 30 minutes. The acid (60% yield) separated after acidification with 10% sulfuric acid and crystallized from ethanol-benzene in needles; ms: m/e (relative intensity) M^+ 280 (100), 279 (14), 265 (2), 264 (7), 263 (29), 237 (5), 236 (25), 235 (5), 234 (16), 229 (4), 203 (3), 202 (8), 191 (10), 189 (7), 165 (3), 146 (2), 145 (6), 140 (5), 134 (3), 121 (7), 118 (3), 117 (4), 115 (3), 104 (3), 102 (3), 101 (3), 89 (10), 77 (6).

3,5-Diarylthiophene-2-carboxylic Acid Piperidides or Morpholides (Tables III and IV).

A suspension of 3-bromo-4,6-diaryl-2*H*-thiopyran-2-one (0.5 g., 0.0015 mole) in methanol (8 ml.) was heated with piperidine or morpholine (1 ml.) on a water bath for 20 minutes. The thiophene amides (75% yield) which separated were crystallized from methanol in needles. Compounds **12a,b** were also prepared by treatment of 3,5-diphenylthiophene-2-

carboxylic acid chloride with piperidine or morpholine; ms: m/e (relative intensity) (compound **12b**) M^+ 349 (57), 348 (3), 317 (5), 265 (12), 264 (41), 263 (100), 262 (3), 237 (4), 236 (21), 235 (9), 234 (20), 203 (13), 192 (3), 191 (13), 190 (4), 189 (8), 166 (4), 132 (3), 121 (3), 116 (3), 101 (2), 89 (5), 77 (3).

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