Synthesis and Fluorescence of 2*H*-Pyrone Derivatives for Organic Light-emitting Diodes (OLED)

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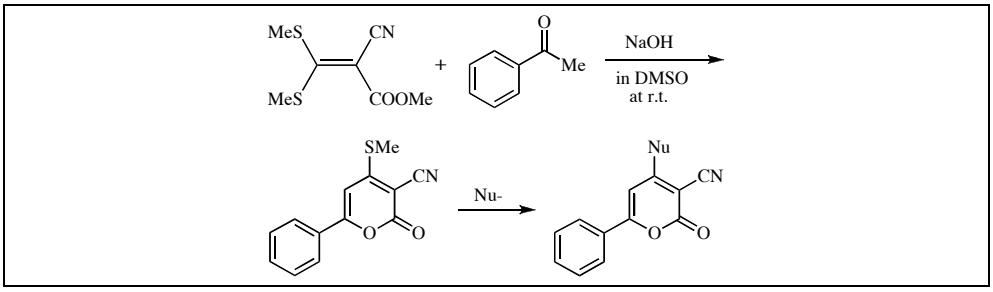

2*H*-Pyrone derivatives were synthesized through the reaction of aryl acetyl compounds with ketene dithioacetals in the presence of sodium hydroxide, and they showed very strong fluorescence in the solid state. The light-emitting region of these 2*H*-pyrones is 447-630 nm in the solid states.

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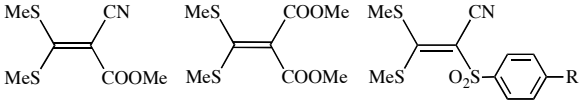
INTRODUCTION

Fluorescent dyes which show fluorescence in the solid state have attracted attention as candidate materials for emitters in electroluminescent (EL) devices [1]. Several of the 4*H*-pyrone derivatives have already been shown to have interesting organic electroluminescence properties [2]. This suggested to us that 2*H*-pyrones might have red electroluminescence, which has been very difficult to harness. We first investigated the 6-aryl-2*H*-pyran-2-ones, expecting them to have superior red fluorescence. Komatsu, *et al*. has indicated that the phenyl group at position 6 in 3,4,6-triphenyl-2*H*-pyrones is an important functional group for fluorescence in these compounds [3]. However, our experiments showed that the substitution of the phenyl group at position 6 in the 2*H*-pyrone ring did not improve the fluorescence. In this study, no derivatives except those with the phenyl group at position 3 and 4 in the 2-pyrone moiety showed any fluorescence.

Here, we will discuss the structure-activity relationships for each functional group at each position in these 2*H*-pyrones and compare with them. In addition, we will discuss the fluorescence activity of some of the related 6-styryl-2*H*-pyran-2-ones. These compounds, which show fluorescence in the solid state, have attracted attention as potential electroluminescence (EL) sources. On 1975, it was reported for the first time that 2*H*-pyrone derivatives were easily obtained through the reaction of ketene dithioacetals with active methylene or methyl compounds in the presence of potassium hydroxide as the base [4]. However, in our experiments, fluorescence was not among the observed chemical and physical properties of the investigated pyrone derivatives. Since some interesting findings were obtained in our reexamination of fluorescence of 2*H*-pyrone derivatives in the solid state, they are reported here.

Synthesis of 2*H*-pyrones. The usefulness of ketene dithioacetal derivatives for the synthesis of heterocyclic compounds has already clarified by the author, who has shown many examples hitherto [4,5].

In this study, in order to elucidate the structure-activity relationships for each substituent and each pyrone derivative, and to clarify the differences in effect between the various types of aryl groups at position 6 of the 2-pyrones and the various substituents on the aryl group, many more derivatives were required than in the last study. Therefore, many new pyrone derivatives were synthesized in this study, and the method of synthesizing 2*H*-pyrone derivatives was also slightly improved.



1a **1b** **1c**; R=H, **1d**; R=Me

Figure 1. Ketene Dithioacetals.

A convenient method of producing 6-aryl- or 6-styryl-4-methylthio-2-oxo-2*H*-pyran-3-carbonitriles and 3-carboxylates through the reaction of various methyl-ketones with ketene dithioacetals, methyl 3,3-

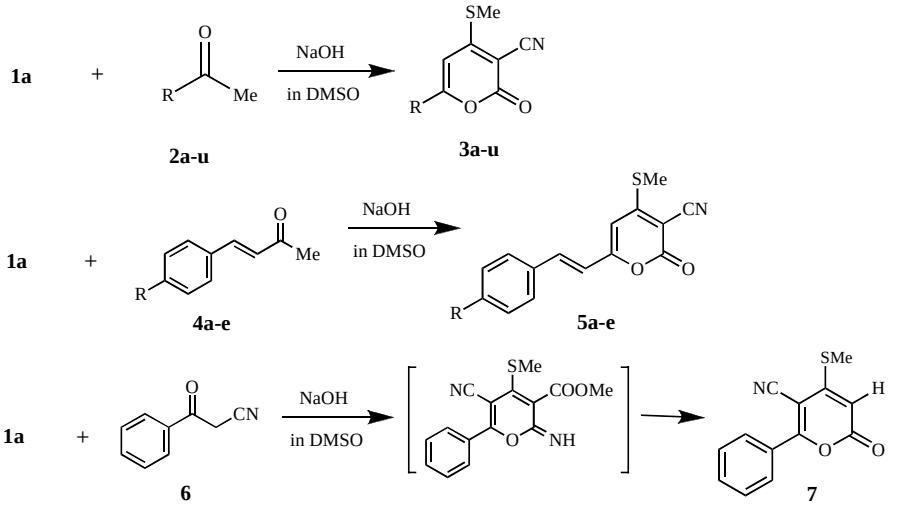
bis(methylthio)acrylonitrilate (**1a**) and dimethyl bis(methylthio)malonate (**1b**) has been reported previously [4,5]. These reactions occur smoothly in the presence of potassium hydroxide as the base and DMSO (dimethyl sulfoxide) as the solvent. In this study, however, the reaction was carried out in the presence of sodium hydroxide as the base to obtain a slightly better yield. The acetyl compounds used in this study were acetophenone (**2a**), 2-methoxyacetophenone (**2b**), 3-methoxyacetophenone (**2c**), 4-methoxyacetophenone (**2d**), 2,4-dimethoxyacetophenone (**2e**), 2,5-dimethoxyacetophenone (**2f**), 3,4-dimethoxyacetophenone (**2g**), 3,4,5-trimethoxyacetophenone (**2h**), 4-dimethylaminoacetophenone (**2i**), 4-bromoacetophenone (**2j**), 2-chloroacetophenone (**2k**), 4-chloroacetophenone (**2l**), 4-phenylacetophenone (**2m**), 4-cyanoacetophenone (**2n**), 1-acetylnaphthalene (**2o**), 2-acetylnaphthalene (**2p**), 3-acetylpyridine (**2q**), 2-acetylthiophenone (**2r**), 2-acetylbenzothiophenone (**2s**), 2-acetylfuran (**2t**), and 5-methyl-2-acetylfuran (**2u**).

The synthesis of 6-aryl-4-methylthio-2*H*-pyran-2-ones (**3a**-**u**) proved to be useful in the preparation of red-fluorescence compounds, which are the most important and the most difficult to produce in the field of electroluminescence. Fortunately, we were able to produce 6-(4-aminophenyl)-2-oxo-2*H*-pyran-3-carbonitriles (**5c-e**), which showed red fluorescence, from 4-(*N*,*N*-disubstituted aminophenyl)but-3-en-2-ones(**4c-e**) and **1a**.

On the other hand, 4-methylthio-6-phenyl-2-oxo-2*H*-pyran-5-carbonitrile (**7**), which is a positional isomer of the cyano group of **3a**, was obtained through the reaction of benzoylacetonitrile (**6**) with **1a** in the presence of sodium hydroxide in DMSO. However, the yield was very low (12%).

We expected methyl 6-aryl-2-oxo-2*H*-pyran-3-carboxylates (**8**) and 3-sulfonyl-2-oxo-2*H*-pyran derivatives (**9**) to have good fluorescence properties as well. 6-Aryl-2-oxo-2*H*-pyran-3-carboxylates (**8a**,**d**) were obtained from **1b** and acetophenone (**2a**) or 4-methoxyacetophenone (**2d**) in a manner similar to the synthesis of 6-aryl-4-methylthio-2*H*-pyran-2-ones (**3a**-**u**). The synthesis of these sulfonyl compounds was carried out through the reaction of sulfonyl ketene dithioacetal (**1c**, **1d**) with **2**. However, the desired 3-

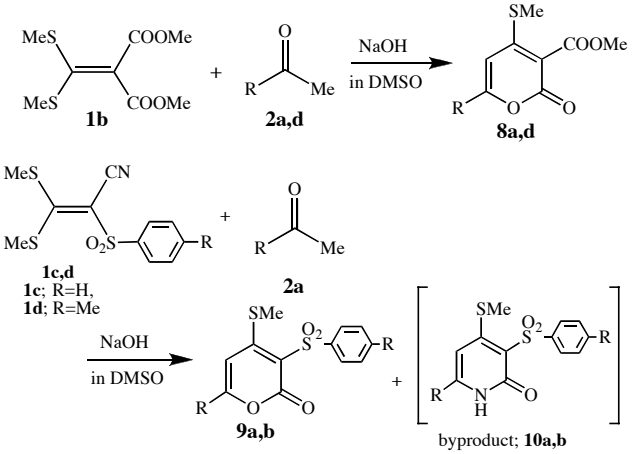
Scheme 1. Synthesis of 6-Aryl-4-methythio-2-oxo-2*H*-pyran-3-carbonitriles



	R	yield(%)		R	yield(%)
3a :	C_6H_5	61	**3o** :	1-naphtyl	63
3b :	C_6H_4-OMe(2)	58	**3p** :	2-naphtyl	75
3c :	C_6H_4-OMe(3)	53	**3q** :	3-pyridyl	58
3d :	C_6H_4-OMe(4)	64	**3r** :	2-thienyl	68
3e :	C_6H_3-$(OMe)_2$(2,4)	33	**3s** :	2-benzothienyl	84
3f :	C_6H_3-$(OMe)_2$(2,5)	27	**3t** :	2-furyl	30
3g :	C_6H_3-$(OMe)_2$(3,4)	40	**3u**	2-furyl-Me(5)	44
3h :	C_6H_2-$(OMe)_3$(3,4,5)	56			
3i :	C_6H_4-NMe_2(4)	85	**5a** :	H	35
3j :	C_6H_4-Br(4)	42	**5b** :	OMe	43
3k :	C_6H_4-Cl(2)	65	**5c** :	NMe_2	32
3l :	C_6H_4-Cl(4)	44	**5d** :	NEt_2	26
3m :	C_6H_4-Ph(4)	88	**5e** :	NPh_2	29
3n :	C_6H_4-CN(4)	66			

phenylsulfonyl-2*H*-pyran-2-one derivative was not obtained through the reaction of **2a** with sulfonyl ketene dithioacetal, ethyl 2-benzenesulfonyl-3,3-bis(methylthio)acrylate, under similar reaction conditions. Lucky, this problem was easily solved by using a different sulfonyl ketene dithioacetal (**1d**). Compound **1e** was allowed to react with **2a** in the presence of sodium hydroxide in DMSO followed by treatment with hydrochloric acid to give the desired 3-phenylsulfonyl-2-oxo-2*H*-pyran (**9a**) in 54% yield. The other sulfonyl compounds (**9b**) were synthesized through the reaction of **1d** with **2a** under the same reaction conditions.

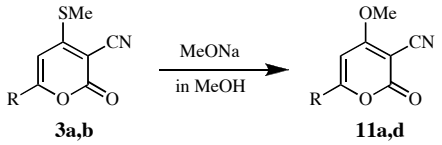
Scheme 2. Synthesis of 6-arly-2-oxo-2*H*-pyran-3-carboxylic acids and 6-arly-3-tolylsulfonyl-2-oxo-2*H*-pyran-3-carbonitriles.



The reaction of **2i** with **1a** was carried out in the presence of sodium hydroxide as the base to obtain the desired product, 6-(4-dimethylaminophenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (**3i**), in 43% yield. The acetyl compounds, 4-(*N,N*-disubstituted aminophenyl)but-3-en-2-ones (**4c-e**) also reacted with **1a** in a manner similar to that described for the preparation of **3a**, and the corresponding 6-[2-(4-*N,N*-disubstituted aminophenyl)vinyl]-4-methylthio-2-oxo-2*H*-pyran-3-carbonitriles (**5c**-**e**) were obtained in 32, 26, and 29% yields, respectively.

In order to obtain strong fluorescent compounds, it is important to give polarity to the molecule 2*H*-pyrone derivatives show strong fluorescence when there is electron-withdrawing group at position 3 and an electron-donating group at position 4. The electron donation property of alkoxy and amino groups at position 4 in 2-pyrone is stronger than that of the methylthio group at the same position. 2-Pyrone derivatives with very high fluorescence can be synthesized, if an alkoxy and an amino group can be introduced at position 4 of 2-pyron. The displacement of **3a**, **3b** and **3c** with a methoxide anion occurred smoothly in the presence of sodium methoxide in methanol to give 4-methoxy-6-phenyl-2-oxo-2*H*-pyran-3-carbonitriles (**11a**, **11d**) in good yields, *i.e*. 61% and 45%, respectively [4].

Scheme 3. Synthesis of 6-arly-4-methoxy-2-oxo-2*H*-pyran-3-carbonitriles.



Next, we will describe the synthesis of 4-amino-6-aryl-2-oxo-2*H*-pyran derivatives. Previously, we have reported the synthesis of 4-amino-6-aryl-2-oxo-2*H*-pyran-3-carbonitriles through the displacement reaction of 4-methylthio-2*H*-pyran-3-carbonitriles with various amines in refluxing methanol. Many 4-amino-6-aryl-2-oxo-2*H*-pyran derivatives (**12a**-**x**) were prepared by this method. The disadvantage of this reaction is that the reaction time is long. We tried a very simple method of synthesizing 4-amino-2*H*-pyrones through the direct reaction of 2-pyrones with amines under heating at 100° for 5-10 minutes without any solvent. This reaction gave a separable mixture of the desired **12a**-**x** and butadiene derivatives (**15a-m**).

It was possible to easily separate this mixture into each chemical compound due to differences in their solubility in methanol. The structure of these butadienes after purification of the crude products were 5-amino-3-methylthio-5-phenyl-penta-2,4-dienitriles (**15a-m**) by the IR, UV, NMR, Ms spectra and elemental analysis. Finally, one of these products (**15b**) was determined by X-ray crystallographic analysis. Figure 2 shows the ORTEP drawings of the crystal structure.

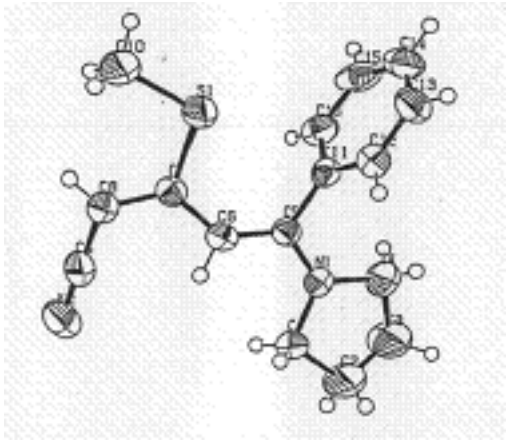
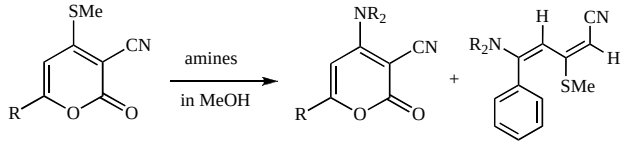


Figure 2. ORTEP Drawing of **15b**.

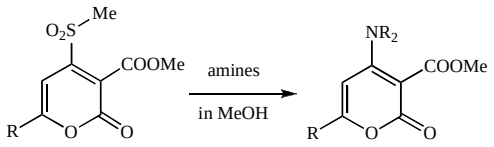
Methyl 4-amino-6-aryl-2-oxo-2*H*-pyran-3-carboxylates (**14a**-**f**) were prepared using the method reported by us previously. The compounds (**13a**, **13b**) were allowed to react with amines (methylamine, benzylamine,

dimethylamine, pyrrolidine) under refluxing methanol to give **14a**-**f** in good yields.

Scheme 4. Synthesis of 4-Amino-6-aryl-2-oxo-2*H*-pyrans.



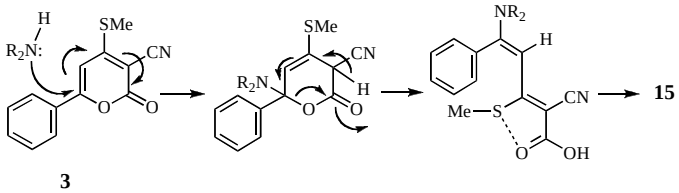
3a,**c**,**d**,**f**,**g**,**h**,**j**,**k**,**o**,**r**,**s** **12a-x** **15a**,**b**,**e**,**f**,**h**,**l**,**m**,**p**



13a, b **14a-f**

	R	NR_2	**12**: yield(%)	**15**: yield(%)
a :	C_6H_5	dimethyamino	29	48
b :	C_6H_5	pyrrolidino	52	38
c :	C_6H_5	morpholino	48	-
d :	C_6H_4-OMe(3)	dimethyamino	40	-
e :	C_6H_4-OMe(4)	dimethyamino	50	47
f :	C_6H_4-OMe(4)	pyrrolidino	51	30
g :	C_6H_4-OMe(4)	morpholino	42	-
h :	C_6H_4-OMe(4)	thiomorpholino	38	22
i :	C_6H_4-OMe(4)	phenethylamino	60	-
j :	C_6H_3-$(OMe)_2$(2,5)	morpholino	78	-
k :	C_6H_3-$(OMe)_2$(3,4)	morpholino	69	-
l :	C_6H_4-NMe_2(4)	dimethyamino	64	28
m :	C_6H_4-NMe_2(4)	pyrrolidino	44	51
n :	C_6H_4-NMe_2(4)	morpholino	50	-
o :	C_6H_4-NMe_2(4)	thiomorpholino	58	-
p :	C_6H_4-Br(4)	pyrrolidino	53	29
q :	C_6H_4-Cl(2)	morpholino	93	-
r :	C_6H_4-Cl(4)	pyrrolidino	46	-
s :	C_6H_4-Ph(4)	pyrrolidino	44	-
t :	1-naphtyl	pyrrolidino	86	-
u :	1-naphtyl	morpholino	88	-
v :	2-thienyl	pyrrolidino	58	-
w :	2-thienyl	morpholino	47	-
x :	2-benzothienyl	pyrrolidino	53	-
			14: yield(%)	
14a :	C_6H_5	methylamino	95	
14b :	C_6H_5	benzylamino	75	
14c :	C_6H_5	dimethyamino	98	
14d :	C_6H_4-OMe(4)	methylamino	95	
14e :	C_6H_4-OMe(4)	dimethyamino	72	
14f :	C_6H_4-OMe(4)	pyrrolidino	72	

Scheme 5. Reaction Pathway of **15**



RESULTS AND DISCUSSION.

An efficient method of measuring fluorescence must be used in order to obtain the exact fluorescence intensities of many 2-pyrone derivatives. It is very easy to find the fluorescence of the corresponding compounds in the solid state: simple irradiation with a hand-held UV lamp (254 nm) as the first stage of a screening test is sufficient for obtaining the corresponding fluorescence values. In our study, we first placed the compounds on filter paper then we irradiated them with a UV lamp, and we assessed their fluorescence with the naked eye. The fluorescence intensities were divided into 6 categories. By defining AlQuinoline$_3$ (AlQ_3) as the standard compound, the fluorescence intensities of the other 2-pyrone derivatives were determined. The results are shown in Table 1.

Table 1. Eye-measuring of 6-aryl-2-oxo-2*H*-pyrans

Intensity	Compound No.
5	**3b, 3d, 3f, 8d, 9b, 12d, 12e, 12f, 12g, 12h, 12k, 12m, 12n, 12r, 12u**
4	**3a, 3g, 3l, 3m, 3r, 11a, 12a, 12i, 12u, AlQ_3**
3	**3i**
2	**3t, 3u**
1	**14b**
0	**3n, 7**

Next, a secondary evaluation of the fluorescence of these 2*H*-pyrones was carried out using a fluorophotometer. The measurement of the absorption and fluorescence spectra was carried out in ethanol solution and in the solid state, respectively, at room temperature. The spectroscopic properties, absorption maxima (λ_{max}), molar absorption (ε), fluorescence maxima (λ_{max}), and relative fluorescence intensities (R.I.) are listed in Table 2-4.

Table 2. Spectral data of 6-Aryl-2-oxo-2*H*-pyrans (**3**, **5**).

No.	UV λ max(log ε) nm(EtOH)	Ex max nm(solid)	Em max nm(solid)	SS[a]	R.I.[b]
3a	328(4.24)	358	480	122	1.54
3b	387(4.35)	357	493	136	1.67
3c	369(4.29)	350	495	145	1.16
3d	395(4.45)	297	536	239	1.23
3e	400(4.60)	297	534	237	0.57
3f	402(4.28)	303	531	228	0.71
3g	402(4.39)	294	551	257	0.76
3h	391(4.33)	295	502	207	0.28
3i	465(4.58)	301	608	307	0.15
3j	337(4.33)	304	518	214	0.76
3k	354(4.18)	296	491	195	0.68
3l	336(4.34)	364	492	128	1.29
3m	388[c]	326	509	183	1.11
3n	332(4.12)	0.00	0.00	-	0.00
3o	371(4.22)	303	498	195	0.66
3p	370(4.17)	342	516	174	2.01
3q	327(4.24)	297	468	169	0.06
3r	415(4.30)	309	563	254	0.84
3s	408(4.40)	298	543	245	0.37
3t	395(4.42)	323	546	223	0.59
3u	404(4.47)	298	521	223	0.21
5a	395[c]	323	541	218	0.39

Table 2 (continued)

No.	UV λ max(log ε) nm(EtOH)	Ex max nm(solid)	Em max nm(solid)	SS[a]	R.I.[b]
5b	415(4.30)	309	563	254	0.84
5c	513(4.67)	342	699	357	0.01>
5d	529(4.69)	346	705	359	0.01>
5e	502(4.19)	349	645	296	0.01>

[a] Stoke's Shift=Em(solid)-Ex(solid). [b] Relative intensity of fluorescence in solid state, usingAlQ_3 as a stadard. [c] insufficient solubility. [d] amorphus

important, materials which emit blue light are the most fundamental and those which emit red light are the most difficult to synthesize. In comparison with the spectroscopic properties of 4-methylthio-2-oxo-6-phenyl-2*H*-pyran-3-carbonitriles (**3a-u**), both the absorption and the fluorescence maxima of 2-pyrones bearing electron-rich aryl groups showed longer wavelength shifts, together with an increase in molar absorption. The aryl group at position 6 of the 2-pyrone derivatives was also found to contribute to the fluorescence. Our study showed

Table 3. Spectral data of 6-Aryl-2-oxo-2*H*-pyrans (**8**, **9, 14**).

No.	R, R', NR2	UV λ max(log ε) nm(EtOH)	Ex max nm(solid)	Em max nm(solid)	SS[a]	R.I.[b]
8a	R=C_6H_5	360(4.18)	299	475	176	6.31
8d	R=C_6H_5-OMe(4)	386(4.41)	295	483	188	3.94
9a	R=C_6H_5, R'=H	339(4.28)	297	460	163	0.51
9b	R=C_6H_5, R'=Me	387(4.54)	294	508	214	11.27
14a	R=C_6H_5, NR_2=methylamino	314(4.26)	296	437	141	3.51
14b	R=C_6H_5, NR_2=benzylamino	305(4.28)	272	445	173	0.96
14c	R=C_6H_5, NR_2=dimethylamino	303(4.28)	272	453	181	0.27
14d	R=C_6H_5-OMe(4), NR_2=methylamino	341(4.38)	270	453	183	1.46
14e	R=C_6H_5-OMe(4), NR_2=dimethylamino	321(4.41)	258	457	199	9.81
14f	R=C_6H_5-OMe(4), NR_2=pyrrolidino	311(4.46)	265	466	201	3.87

Table 4. Spectral data of 6-Aryl-2-oxo-2*H*-pyrans (**11**, **12**).

No.	R	position 4	UV λ max(log ε) nm(EtOH)	Ex max nm(solid)	Em max nm(solid)	SS[a]	R.I.[b]
11a	a; C_6H_5	methoxy	320(4.18)	367	472	105	2.88
11d	e; C_6H_4-OMe(4)	methoxy	376(4.49)	375	487	112	5.14
12a	a; C_6H_5	dimethylamino	310(4.35)	361	447	86	1.50
12b	b; C_6H_5	pyrrolidino	308(4.36)	304	478	174	0.91
12c	c; C_6H_5	morpholino	315(4.41)	371	455	99	3.08
12d	d; C_6H_4-OMe(3)	dimethylamino	324(4.25)	303	476	173	0.92
12e	e; C_6H_4-OMe(4)	dimethylamino	332(4.42)	376	475	99	6.90
12f	f; C_6H_4-OMe(4)	pyrrolidino	331(4.41)	369	453	84	4.27
12g	g; C_6H_4-OMe(4)	morpholino	336(4.43)	374	475	101	4.60
12h	h; C_6H_4-OMe(4)	thiomorpholino	339(4.47)	373	474	101	4.14
12i	j; C_6H_4-OMe(4)	phenethylamino	346(4.42)	370	461	91	4.34
12j	k; C_6H_3-$(OMe)_2$(2,5)	morpholino	364(4.15)	371	509	138	3.05
12k	l; C_6H_3-$(OMe)_2$(3,4)	morpholino	358(4.25)	296	497	201	5.52
12l	n; C_6H_4-NMe_2(4)	dimethylamino	400(4.57)	294	517	223	9.90(5.72[d])
12m	o; C_6H_4-NMe_2(4)	pyrrolidino	396(4.64)	373	537	164	3.86
12n	p; C_6H_4-NMe_2(4)	morpholino	409(4.54)	322	606	284	1.08
12o	q; C_6H_4-NMe_2(4)	thiomorpholino	410(4.57)	295	582	287	0.43
12p	r; C_6H_4-Br	pyrrolidino	315(4.42)	363	516	153	1.45
12q	s; C_6H_4-Cl(2)	morpholino	298(4.17)	303	466	163	0.78
12r	t; C_6H_4-Cl(4)	pyrrolidino	314(4.38)	369	481	112	2.84
12s	u; C_6H_4-Ph	pyrrolidino	328(4.56)	352	479	127	1.28
12t	v; 1-naphtyl	pyrrolidino	320(4.30)	359	470	111	1.38
12u	w; 1-naphtyl	morpholino	324(4.33)	361	472	111	1.43
12v	x; 2-thienyl	pyrrolidino	336(4.36)	369	486	117	2.51
12w	y; 2-thienyl	morpholino	343(4.57)	375	461	116	6.99
12x	z; 2-benzothienyl	pyrrolidino	349(4.45)	369	494	125	1.81

The discovery of intensely fluorescent materials emitting light in the three primary colors (red, green and blue; RGB) is crucial for the development of organic EL materials. The three primary colors are RGB, and their light-emission wavelengths are 440 nm, 550 nm, and 630 nm, respectively. Although each primary color is

that the fluorescence of 6-methyl-2-oxo-2*H*-pyran-3-carbonitrile was very week [4]. Among the 6-phenyl-2-pyrone derivatives, those with electron-donating groups on the phenyl group (**3a-c**) showed the strongest fluorescence. Compound **3a**, which had an unsubstituted phenyl group at position 6, emitted light in the shortest

wavelength region (480 nm). The light-emission region was found to shift toward the longer-wavelength side when, a methoxy group was introduced as the electron-donating group on the phenyl group. On the other hand, compound **3d** emitted light at 536 nm, when a methoxy group was introduced at position 4 on the phenyl group; its light-emitting region was 56 nm further toward the red side than that of **3a**. The shift toward the longer-wavelength side was slight considering the parting of the localized system of the conjugated system between the methoxy group at position 2 on phenyl group and the pyrone ring by steric hindrance in **3b**. In the case of **3c** however, there was no shift toward the longer wavelength side because of the weak electronic effect of the meta-position of the methoxy group. The fluorescence maxima of 6-(4-dimethylaminophenyl)-2-oxo-2*H*-pyran-3-carbonitrile (**3i**) appeared at 608 nm (R.I. = 0.15), which is close to the red light region. Red fluorescence dyes are currently of great interest in various fields, and are expected to be used as emitters in electroluminescent devices. In this type of application, red light emission around 620-640 nm is anticipated for the light-emitting materials to be used in EL devices.

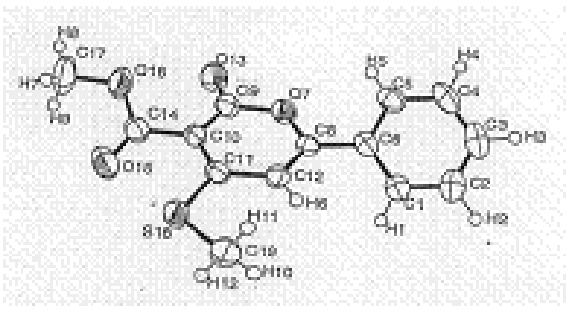
Compound **3n**, which bears a cyano group as the electron-withdrawing substituent, did not emit any light. Similarly, electron-deficient hetero aryl compounds such as 6-pyrid-3-yl-2*H*-pyrone (**3q**) emitted very weak light.

The naphthyl and hetero aryl derivatives (**3o**, **3p**, **3r**-**u**) also showed moderate fluorescence (Table 2). The light-emission region of **3o** (498 nm) shifted downward by 18 nm due to the twisting caused by steric hindrance with both the naphthyl and the pyranyl group. The light-emission regions of compounds **3r-u** shifted toward the longer-wavelength side (563, 543, 546, and 521 nm, respectively), even when the aromatic substituent at position 6 was changed to an electron-rich heterocyclic compound. Notably, 6-thien-2-yl-2*H*-pyrone (**3r**) emitted light at 563 nm. The styryl-2*H*-pyrone derivatives (**5a**-**e**) introduced at the double bond between the aryl group at position 6 and the pyrone ring can be supposed to emit light of longer-wavelengths. 6-Styryl-4-methylthio-2*H*-pyrone (**5a**) emitted light at 541 nm and the methoxy derivative (**5b**) emitted light at 563 nm. The light emission of this amino styryl (**5c-e**) was not as strong when it was in crystal form. We found that the aryl and the styryl group at position 6 of the pyrone derivatives had the greatest effect on the fluorescence of the pyrone compounds.

Next in importance is the effect of the electron-donating substituent at position 4 and the electron-withdrawing substituent at position 3. The light emission was intense in the 2*H*-pyrones with electron donating substituents at position 4. It is said that sulfur atoms in fluorescent compounds generally weaken the fluorescence [6]. Therefore, we expected the compounds to show stronger fluorescence when the methylthio group at position 4 was substituted by an alkoxy or an amino group. The fluorescences of the alkoxy and the amino derivatives were considerably stronger than that of the methylthio compounds. The light-emission region showed a 40-50 nm blue shift. The 4-amino compound (**12a**) emitted a typically blue fluorescent light (447 nm), as shown in Table 4.

However, the position of the cyano group on the pyrone ring is also an important factor of the fluorescent property. Almost all 6-aryl-2-oxo-2*H*-pyran-3-carbonitrile derivatives except **3n** and **3q** showed fluorescence in the solid state as shown in Table 2. Only, 2-oxo-6-phenyl-2*H*-pyran-5-carbonitrile (**7**) showed absolutely no fluorescence. This suggested to us that the position of the electron-deficient group in the 2-pyrone derivatives is crucial for electroluminescence.

Inserting an ester or a sulfonyl group at position 3 of the 2-pyrones is also an effective way of inducing the fluorescence in the solid state. The fluorescence was more intense than that of the corresponding cyano compounds. Remarkably, the fluorescence of the sulfonyl compound (**9b**) was 11 times higher than that of the standard compound (AlQ_3). Contrary to expectations, the electron-withdrawal seems not to be the cause of this phenomenon. A detailed structural analysis of **8a** was carried out using X-ray crystallography (Figure 3, 4). The intra-molecular distances between the non-bonded S and O (SMe…COOMe) was 2.735 Å, which is smaller than the sum of the van der Waals radii of O and S (3.25 Å). Similar strong interactions have been reported previously for other compounds, and the distances were in the range of 2.41-2.78 Å. The distance between the non-bonded O and O (COOMe…C=O) was determined in ORTEP to be 2.713 Å. The eight central atoms, S(18), C(7), C(8), C(9), C(10), C(11), C(12), and C(14), were almost planar. The molecules were stacked along the *c*-axis due to their π–π interaction force. The shortest intermolecular distance was 3.345 Å between O(13) and C(5), which would reflect the distance of the charge transfer complex in chloranyl-tetramethyl *p*-phenylendiamine (3.26 Å).



Figures 3. ORTEP Drawing of **8a**.

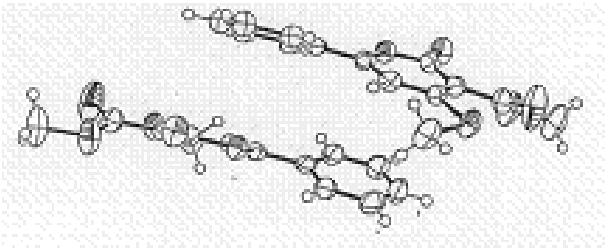
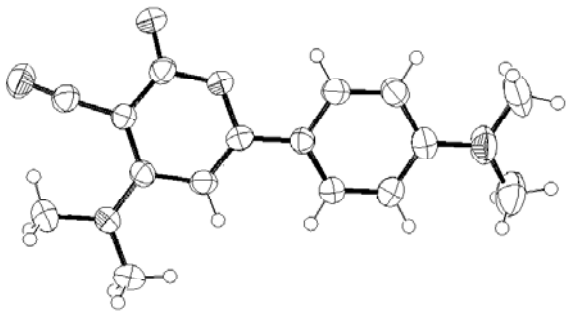
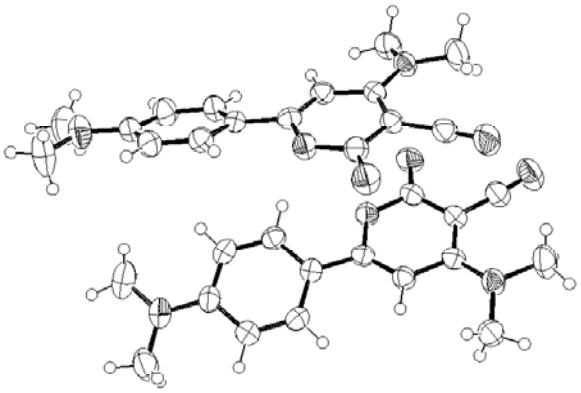


Figure 4. Asymmetric unit of **8a**.

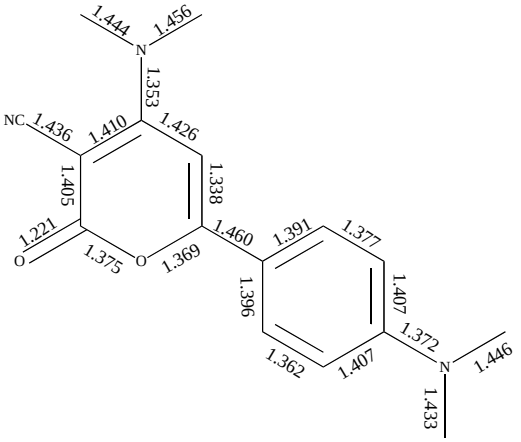
In the present study, the pyrone derivatives showed almost no fluorescence in solution, although these compounds showed strong fluorescence in the solid state. Remarkably, 4-dimethylamino-6-(4-dimethylaminophenyl)-2-oxo-2*H*-pyran-3-carbonitrile (**12l**), 6-(4-*N*,*N*-dimethylaminophenyl)-4-morpholino-2-oxo-2*H*-pyran-3-carbonitrile (**12n**) and 6-(4-dimethylaminophenyl)-4-pyrrolidino-2-oxo-2*H*-pyran-3-carbonitrile (**12m**), also showed strong fluorescence in ethanol, and the fluorescent quantum yields were 0.57, 0.45, and 0.70 respectively. These compounds will be utilized as fluorescent materials in an oxalate chemiluminescence system [7]. A detailed structural analysis of **12l** was carried out using X-ray crystallography (Figure 5-8). The shortest intermolecular distance in 4-amino-6-(4-dimethylamino-phenyl)-2*H*-pyrone was found to be 3.120 Å between O(13) and N(37). In addition, because the intermolecular distances between O(13) and C(32) and between O(13) and C(38) are 3.236 Å and 3.293 Å respectively, intermolecular π electron interaction can take place. Moreover, we think that the array of molecules resembles the CT complex because the intermolecular distance of the CT complex is 3.21 Å, and that a very strong π electron interaction works because the shortest intramolecular distance is 3.120 Å. We speculate that the dimethylamino group at position 6 of the phenyl group and the dimethylamino group at position 4 of the pyrone ring are almost planar due to their torsion angles. On the other hand, it appears that the angle of twisting between the pyrone ring and a phenyl ring bearing the dimethylamino group was approximately 10 degrees. Moreover, **12l** has a structure that allows easy intramolecular charge movement, as shown in Figure 9; we believe that it is a betaine structure which might explain the uncommonly strong fluorescence.



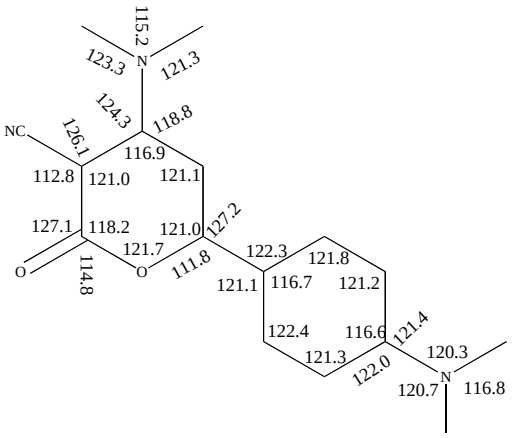
Figures 5. ORTEP Drawing of **12l**.



Figures 6. Asymmetric unit of **12l**.



Figures 7. Bond length(Å) of **12**



Figures 8. Bond angles(°) of **12l**.

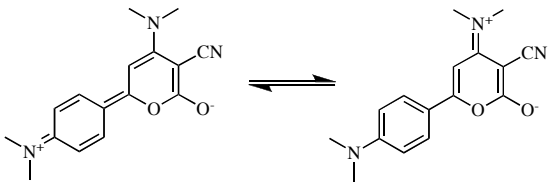
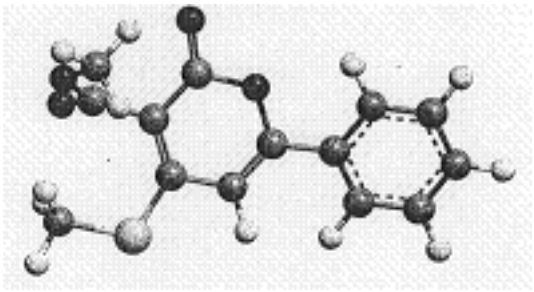


Figure 9. Betaine Strucuture of **12l**.

Lastly, we describe about the twist angle between the aryl and pyranyl groups in these fluorescent 2-pyrans. The aryl group at position 6 on the pyrone ring in compounds showing strong fluorescence was found to be twisted relative to the pyrone ring at angle of 25 degrees. We hypothesized that the angle of twisting is an important factor of fluorescence, and the result of the X-ray crystallographyic analysis (ORTEP) suggests that the structure with minimum energy in the ground state has a twist angle of 25 degrees. These results agree well with the results of our calculations using MOPAC and Stork's shift in our measurement analysis. The optimized molecular structure of **8a** was calculated by using MOPAC (AM1), as summarized in Figures 10. It is reasonable to assume that the design of fluorescent materials will be possible if the correlation between the relative fluorescence intensity and the HOMO and LUMO energies is clarified. This is a future research topic.



Figures 10. Calculated structure of **8a** (by MOPAC/AM1).

Conclusion. The 2*H*-pyrone derivatives synthesized through the reaction of aryl acety compounds with ketene dithioacetals in the presence of sodium hydroxide showed very strong fluorescence in the solid state. The light-emitting region of these 2*H*-pyrones was 440-630 nm in the solid state. The structure-activity relationship in these fluorescent 2*H*-pyrone derivatives was also clarified. The presence of an amino group at position 4 on the aryl group shifts the light-emitting region toward shorter wavelengths. 2-Pyrone derivatives bearing an electron-donating group a position 4 and an electron-withdrawing group at position 3 on the 2-pyrone ring are fluorescent both in solution and in the solid state. The aryl group at position 6 on the 2-pyrone ring in compounds showing strong fluorescence was twisted relative to the 2-pyrone ring at an angle of 25 degrees. We believe that this twist angle is an important factor of fluorescence.

EXPERIMENTAL

The identification of compounds and the measurement of their properties were carried out using the following general procedures and equipment. All melting points were determined in a capillary tube and are uncorrected. The infrared (IR) spectra were recorded using potassium bromide pellets on a JASCO 810 or Shimazu IR-460 spectrometer, and the ultraviolet (UV) absorption spectra were determined in 95% ethanol on a Hitachi 323 spectrometer. The fluorescence spectra were determined on Shimazu UV3100. The nuclear magnetic resonance (NMR) spectra were obtained on Gemini 300 NMR (300 MHz) and 500 NMR (500 MHz) spectrometers with tetramethylsilane as the internal standard. The mass spectra (MS) were recorded on JOEL DX-303 mass spectrometers. Microanalyses were performed by H. Mazume on a Yanaco M-5 or Perkin Elmer 2002 at Nagasaki University. All chemicals were reagent-grade and used without further purification unless otherwise specified.

Method of Fluorescence Measurement. ***In the Solid State.*** A powder sample of the subject compound was heaped on a tray. After covering the sample with a quartz plate, the tray was fixed in the fluorescence spectrometer. After setting the fluorescence wavelength, the excitation spectrum was determined through scanning at the fluorescence wavelength. Similarly, the fluorescence spectrum was obtained after scanning at the excitation wavelength. Then, the excitation wavelength was determined and the fluorescence spectrum was measured.

The relative fluorescence intensity was determined using AlQ_3 as the standard sample. The fluorescence of the standard sample and all subject compounds were measured at 272 nm excitation.

In Solution. The fluorescence quantum yields of the subject compounds were compared with those of 9,10-diphenyl-anthracene or anthracene, which was used as the standard. The concentration of the measured samples in the excitation wavelength region was adjusted using a molar absorption coefficient of 0.05. The fluorescence spectra in solution were obtained in a manner similar to that described for the measurement in the solid states. The quantum yields of 9,10-diphenylanthracene and anthracene were ϕ=0.81 and ϕ=0.25 at 366nm and 254 nm excitation, respectively.

4-Methylthio-2-oxo-6-phenyl-2*H*-pyran-3-carbonitrile (3a). A mixture of 10 mmoles of acetophenone **2a** and 10 mmoles of ketenedithioacetal **1a**, 20 mmoles of powdered sodium hydroxide, and 30 ml of DMSO was stirred at room temperature for 3 hours. The reaction mixture was poured into 300 ml of ice-water and the whole was stirred at room temperature for 30 minutes. The yellow precipitates that appeared were collected by filtration, washed with water, and recrystallized from a mixture of toluene and methanol to give 1.48 g (6.1 mmoles) of 4-methylthio-2-oxo-6-phenyl-2*H*-pyran-3-carbonitrile (**3a**) as yellow needles, mp 200-201°, in 61% yield [4]. Previously, we used potassium hydroxide as a base and new compounds were only showed in here. ^{1}H-nmr (deuteriochloroform) δ: 2.82 (s, 3H, SMe), 7.15 (s, 3H, 5-H), 7.52-7.76 (m, 3H, 3', 4' and 5'-H), 7.84-7.99 (m, 2H, 2', 6'-H)[4].

6-(2-Methoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3b). This compound (0.79 g, 2.9 mmoles) was obtained in 58% yield from **1a** (1.02 g, 5.0 mmoles) and **2b** (0.75 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 209-211°; ir (potassium bromide) υ_{max} cm^{-1}: 2200 (CN), 1700 (C=O), 1580, 1550, 1475, 1430, 1330, 1270, 1240, 1160, 1125, 10 50, 1030, 1005; uv(ethanol) λ max nm (log ε):254 nm (4.22), 317 nm (4.21), 387 nm (4.35); ^{1}H-nmr (deuteriochloroform) δ: 2.67 (s, 3H, SMe), 3.99 (s, 3H, OMe), 7.04 (d, 1H, 6'-H, J=8.5 Hz), 7.11 (dd, 1H,

4'-H, J=7.4, 8.2 Hz), 7.37 (s, 1H, 5-H), 7.52 (dd, 1H, 5'-H, J=8.2, 8.5 Hz), 8.00 (d, 1H, 3'-H, J=7.4 Hz); ms *m/z*: 274 (M^++1, 17), 273 (M^+, 100), 245 (41), 136 (10), 135 (82), 111 (11), 97 (17), 96 (10), 95 (12), 92 (18), 85 (15), 84 (10), 83 (21), 82 (11), 81 (14), 77 (32), 75 (10), 71 (24), 70 (11), 69 (32), 67 (11), 57 (38), 56 (11), 55 (31), 44 (18), 43 (34). *Anal.* Calcd. for $C_{14}H_{11}NO_3S$: C, 61.53; H, 4.06; N, 5.12. Found: C, 61.56; H, 4.19; N, 5.04.

6-(3-Methoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3c). This compound (0.72 g, 2.65 mmoles) was obtained in 53% yield from **1a** (1.02 g, 5.0 mmoles) and **2c** (0.75 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 181-183°; ir(potassium bromide) υ_{max} cm^{-1}: 2210 (CN), 1700 (C=O), 1580, 1480, 1420, 1340, 1290, 1260, 1200, 1180, 1175, 1070; uv(ethanol) λ_{max}nm (log ε): 218 nm (4.36), 254 nm (4.22), 323 nm (4.29), 369 nm (4.29); ^{1}H-nmr(deuteriochloroform) δ: 2.72 (s, 3H, SMe), 3.89 (s, 3H, OMe), 6.70 (s, 1H, 5-H), 7.09-7.13 (m, 1H, 5'-H), 7.38 (d, 1H, 2'-H , J=1.6 Hz), 7.43 (d, 2H, 4', 6'-H, J=5.2 Hz); ms *m/z*: 274 (M^++1, 17), 273 (M^+, 100), 245 (41), 135 (82), 83 (21), 77 (32), 71 (24), 69 (31), 57 (38), 55 (31), 43 (34), 41 (20). *Anal.* Calcd. for $C_{14}H_{11}NO_3S$: C, 61.53; H, 4.06; N, 5.12. Found: C, 61.59; H, 4.10; N, 5.05.

6-(4-Methoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3d). This compound was prepared by the previous method in 64% yield, mp 215°; ^{1}H-nmr(deuteriochloroform) δ; 2.79 (s, 3H, SMe), 3.99 (s, 3H, OMe), 7.09 (s, 1H, 5-H), 7.15 (dd, 2H, 3', 5'-H, J=1.0, 8.0 Hz), 7.99 (dd, 2H, 2', 6'-H, J=1.0, 8.0 Hz)[4].

6-(2,4-Dimethoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3e). This compound (0.50 g, 1.65 mmoles) was obtained in 33% yield from **1a** (1.02 g, 5.0 mmoles) and **2e** (0.90 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 220-222°; ir(potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1715 (C=O), 1610, 1580, 1555, 1480, 1460, 1320, 1280, 1250, 1205, 1180, 1125, 1050, 1015; uv(ethanol) λ_{max}nm (log ε): 259 nm (4.31), 326 nm (4.18), 343 nm (4.25), 400 nm (4.60); ^{1}H-nmr(deuteriochloroform) δ:2.65 (s, 3H, SMe), 3.90 (s, 3H, OMe), 3.96 (s, 3H, OMe) 6.54 (d, 1H, 3'-H, J=2.5 Hz), 6.63 (dd, 1H, 5'-H, J=2.5, 8.8 Hz), 7.30 (s, 1H, 5-H), 8.01 (d, 1H, 6'-H, J=8.8 Hz); ms *m/z*: 303 (M^+, 100), 287 (10), 275 (34), 256 (16), 232 (10), 165 (58), 149 (10), 98 (10), 97 (18), 96 (10), 95 (12), 85 (16), 84 (12), 83 (21), 82 (11), 81 (13), 73 (14), 71 (23), 70 (12), 69 (27), 67 (11), 60 (14), 57 (40), 56 (13), 55 (32), 44 (94). *Anal.* Calcd. for $C_{15}H_{13}NO_4S$: C, 59.40; H, 4.32; N, 4.62. Found: C, 59.11; H, 4.62; N, 4.32.

6-(3,4-Dimethoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3g). This compound was prepared by the previous method in 40% yield, mp 221°; ^{1}H-nmr (deuteriochloroform) δ; 2.84 (s, 3H, SMe), 4.04 (s, 6H, OMe), 7.12 (s, 1H, 5-H), 7.16 (d, 1H, 5'-H, J=8.0 Hz), 7.61 (d, 1H, 2'-H, J=1.5 Hz) [4].

6-(2,5-Dimethoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3f). This compound (0.41 g, 1.35 mmoles) was obtained in 27% yield from **1a** (1.02 g, 5.0 mmoles) and **2f** (0.90 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 225-226°; ir (potassium bromide) υ_{max} cm^{-1}: 3150, 2920, 2820, 2220 (CN), 1695 (C=O), 1560, 1480, 1360, 1310, 1260, 1250, 1230, 1190, 1165, 1130, 1050, 1010; uv(ethanol) λ_{max}nm (log ε): 221 nm (4.51), 254 nm (4.17), 323 nm (4.29), 402 nm (4.28); ^{1}H-nmr (deuteriochloroform) δ: 2.66 (s, 3H, SMe), 3.83 (s, 3H, OMe), 3.94 (s, 3H, OMe), 6.97 (d, 1H, 4'-H, J=9.1 Hz), 7.07 (dd, 1H, 3'-H, J=3.3, 9.1 Hz), 7.43 (s, 1H, 5-H), 7.49 (dd, 1H, 6'-H, J=3.3 Hz); ms *m/z*: 304 (M^++1, 18), 303 (M^+, 100), 275 (10), 165 (49), 107 (10), 275 (10), 57 (15), 55 (12), 44 (22), 43 (14). *Anal.* Calcd. for $C_{15}H_{13}NO_4S$: C, 59.40; H, 4.32; N, 4.62. Found: C, 59.28; H, 4.35; N, 4.49.

6-(3,4,5-Trimethoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3h). This compound (0.93 g, 2.8 mmoles) was obtained in 56% yield from **1a** (1.02 g, 5.0 mmoles) and **2h** (1.05 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow leaflets, mp 208-210°; ir (potassium bromide) υ_{max} cm^{-1}: 2205 (CN), 1720(C=O), 1630, 1590, 1570, 1480, 1420, 1360, 1300, 1250, 1190, 1130, 1085; UV(ethanol) λ_{max}nm (log ε): 391 nm (4.33); ^{1}H-nmr (deuteriochloroform) δ: 2.73 (s, 3H, SMe), 3.94 (s, 9H, OMe), 6.60 (s, 1H, 5-H), 7.04 (s, 2H, 2', 6'-H); ms *m/z*: 345 (M^++1, 20), 333 (M^+, 100), 318 (14), 307 (10), 210 (16), 196 (10), 195 (75), 75 (15), 60 (14), 57 (17), 55 (14), 45 (11), 44 (100). *Anal.* Calcd. for $C_{16}H_{15}NO_5S$: C, 57.65; H, 4.54; N, 4.20. Found: C, 57.28; H, 4.49; N, 4.33.

6-(4-Dimethylamino)phenyl-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3i). This compound (1.22 g, 4.25 mmoles) was obtained in 85% yield from **1a** (1.02 g, 5 mmoles) and **2i** (0.82 g, 5 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give orange needles, mp 249-251°; ir (potassium bromide) υ_{max} cm^{-1}: 2200 (CN), 1700 (C=O), 1610, 1575, 1525, 1380, 1355, 1205; uv(ethanol) λ_{max}nm (log ε): 465 nm (4.58); ^{1}H-nmr (deuteriochloroform) δ: 2.66 (s, 3H, SMe), 3.11 (s, 6H, 2xNMe$_2$), 6.47 (s, 1H, 5-H), 6.69 (d, 2H, 3', 5'-H, J=9.0 Hz), 7.75 (d, 2H, 2', 6'-H, J=9.0 Hz); ms *m/z*: 287 (M^++1, 20), 286 (M^+, 100), 285 (10), 258 (27), 215 (10), 183 (12), 148 (54), 77 (10), 44 (15), 42 (11). *Anal.* Calcd. for $C_{15}H_{14}N_2O_2S$: C, 62.92; H, 4.93; N, 9.76; S, 11.20. Found: C, 62.91; H, 4.95; N, 9.77; S, 11.16.

6-(4-Bromophenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3j). This compound was prepared by the previous method in 42% yield, mp 230°; ^{1}H-nmr(deuteriochloroform) δ; 2.81 (s, 3H, SMe), 7.18 (s, 1H, 5-H), 7.40 (d, 2H, 3', 5'-H, J=8.0 Hz), 7.95 (d, 2H, 2', 6'-H, J=8.0 Hz)[4].

6-(2-Chlorophenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3k). This compound (0.90 g, 3.25 mmoles) was obtained in 65% yield from **1a** (1.02 g, 5 mmoles) and **2k** (0.77 g, 5 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 185-186°; ir (potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1720 (C=O), 1605, 1495, 1440, 1340, 1320, 1280, 1260, 1180, 1080, 1040; uv(ethanol) λ_{max}nm (log ε): 240 nm (4.23), 314 nm (4.29), 354 nm (4.18); ^{1}H-nmr (deuteriochloroform) δ: 2.68 (s, 3H, SMe), 6.93(s, 1H, 5-H), 7.43-7.56(m, 3H, 4', 5' and 6'-H), 7.75(dd, 1H, 3'-H, J=1.9, 7.7 Hz); ms *m/z*: 279 (M^++2, 39), 278 (M^++1, 17), 277 (M^+,100), 251 (24), 249 (65), 139 (91), 111 (48), 75 (42), 57 (26), 44 (15), 43 (20). *Anal.* Calcd. for $C_{13}H_8NO_2SCl$: C, 56.22; H, 2.90; N, 5.04. Found: C, 56.24; H, 3.09; N, 4.97.

6-(4-Chlorophenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3l). This compound was prepared by the previous method in 44% yield, mp 240°; ^{1}H-nmr (deuteriochloroform) δ:

2.73 (s, 3H, SMe), 6.86 (s, 1H, 5-H), 7.58 (dd, 2H, 3', 5'-H, J=1.0, 8.0 Hz), 7.91 (dd, 2H, 2', 6'-H, J=1.0, 8.0 Hz) [4].

6-(2-Biphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3m). This compound (1.40 g, 4.4 mmoles) was obtained in 88% yield from **1a** (1.02 g, 5.0 mmoles) and **2m** (0.98 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow leaflets, mp 273-275°; ir (potassium bromide) υ_{max} cm^{-1}: 3100, 2275, 2210 (CN), 1710 (C=O), 1590, 1555, 1480, 1430, 1410, 1345, 1200, 1185, 1060; uv (ethanol) λ_{max} nm: 388, 350, 267, 240; ^{1}H-nmr (deuteriochloroform) δ: 2.75 (s, 3H, SMe), 6.76 (s, 1H, 5-H), 7.38-7.55 (m, 3H, 3", 4" and 5"-H), 7.65 (d, 2H, 2", 6"-H, J=7.2 Hz), 7.75 (d, 2H, 3', 5'-H, J=8.5 Hz), 7.96 (d, 2H, 2', 6'-H, J=8.2 Hz); ms *m/z*: 320 (M^++1, 24), 319 (M^+, 100), 291 (38), 181 (38), 153 (20), 152 (31), 71 (21), 69 (24), 57 (35), 55 (23), 44 (60), 43 (27). *Anal*. Calcd. for $C_{19}H_{13}NO_2S$: C, 71.45; H, 4.10; N, 4.39. Found: C, 71.49; H, 4.29; N, 4.52.

6-(4-Cyanophenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3n). This compound (0.88 g, 3.3 mmoles) was prepared in 66% yield from **1a** (1.02 g, 5.0 mmoles) and **2n** (0.73 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 251-254°; ir (potassium bromide) υ_{max} cm^{-1}: 2235 (CN), 2200 (CN), 1700 (C=O), 1610, 1575, 1525, 1380, 1355, 1205; uv(ethanol) λ_{max}nm (log ε): 259 nm (4.06), 332 nm (4.12), 370 nm (3.96), 450 nm (2.22); ^{1}H-nmr (deuteriodimethylsulfoxide) δ: 2.52 (s, 3H, SMe), 7.40 (s, 1H, 5-H), 8.04 (d, 2H, 2', 6'-H, J=8.7 Hz), 8.24 (d, 2H, 3', 5'-H, J=8.7 Hz); ms *m/z*: 270 (M^++2, 6), 269 (M^++1, 17), 268 (M^+, 100), 253 (12), 241 (12), 240 (77), 197 (19), 166 (14), 149 (29), 130 (66), 102 (55). *Anal*. Calcd. for $C_{14}H_8N_2O_2S$: C, 62.68; H, 3.01; N, 10.44; S, 11.95. Found: C, 62.51; H, 3.13; N, 10.21; S, 11.92.

4-Methylthio-6-(1-naphthyl)-2-oxo-2*H*-pyran-3-carbonitrile (3o). This compound (0.85 g, 2.90 mmoles) was obtained in 58% yield from **1a** (1.02 g, 5.0 mmoles) and **2o** (0.85 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow leaflets, mp 222-224°; ir (potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1700 (C=O), 1585, 1480, 1420, 1390, 1360, 1315, 1260, 1230, 1170, 1020; uv(ethanol) λ_{max} nm(log ε): 289 nm (4.00), 371 nm (4.22); ^{1}H-nmr (deuteriochloroform) δ: 2.68 (s, 3H, SMe), 6.64 (s, 1H, 5-H), 7.54-7.72 (m, 3H, naphthyl 3', 6' and 7'-H), 7.75 (d, 1H, naphthyl 2'-H, J=9.0 Hz), 7.95(dd, 1H, naphthyl 4'-H, J=2.2, 9.0 Hz), 8.05 (d, 1H, naphthyl 8'-H, J=8.0 Hz), 8.15 (dd, 1H, naphthyl 5'-H, J=0.5, 8.4 Hz); Ms *m/z*: 294 (M^++1, 22), 293 (M^+, 100), 265 (38), 155 (57), 127 (61), 71 (21), 57 (31), 44 (22), 43 (22). *Anal*. Calcd. for $C_{17}H_{11}NO_2S$: C, 69.61; H, 3.78; N, 4.77. Found: C, 69.70; H, 3.70; N, 4.83.

4-Methylthio-6-(2-naphthyl)-2-oxo-2*H*-pyran-3-carbonitrile (3p). This compound (1.10 g, 3.75 mmoles) was obtained in 75% yield from **1a** (1.02 g, 5.0 mmoles) and **2p** (0.85 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow leaflets, mp 245-247°; ir (potassium bromide) υ_{max} cm^{-1}: 2225 (CN), 1710 (C=O), 1590, 1490, 1430, 1380, 1345, 1320, 1280, 1190, 1130, 1060; uv(ethanol) λ_{max} nm(log ε): 289 nm (3.96), 299 nm (3.97), 337 nm (4.14), 352 nm (4.15), 370 nm (4.17);^{1}H-nmr(deuteriochloroform)δ: 2.77 (s, 3H, SMe), 6.84 (s, 1H, 5-H), 7.59-7.64 (m, 2H, naphtyl 6', 7'-H), 7.82 (dd, 1H, naphthyl 3'-H, J=1.8, 9.0 Hz), 7.88-7.98 (m, 3H, naphthyl 4', 5' and 8'-H), 8.50 (d, 1Hd, naphthyl 1'-H, J=1.8 Hz); ms *m/z*: 294 (M^++1, 15), 293 (M^+, 64), 265 (32), 155 (100), 127 (82), 69 (48), 75 (20), 69 (20), 57 (34), 55 (22), 44 (24), 43 (29). *Anal*. Calcd.for $C_{17}H_{11}NO_2S$: C, 69.61; H, 3.78; N, 4.77. Found: C, 69.31; H, 3.70; N, 4.83.

4-Methylthio-6-2-oxo-(3-pyridyl)-2*H*-pyran-3-carbonitrile (3q). This compound was prepared by the previous method in 58% yield, mp 192°; ^{1}H-nmr(deuteriochloroform) δ; 2.88 (s, 3H, SMe), 7.50 (s, 1H, 5-H), 8.34 (dd, 1H, 5'-H, J=7.0, 8.0 Hz), 9.06 (d, 1H, 6'-H, J=7.0 Hz), 9.25 (dd, 1H, 4'-H, J=1.0, 8.0 Hz), 9.61 (d, 1H, 2'-H, J=1.0 Hz) [4].

4-Methylthio-2-oxo-6-(2-thienyl)-2*H*-pyran-3-carbonitrile (3r). This compound was prepared by the previous method in 68% yield, mp 253°; ^{1}H-nmr(deuteriochloroform) δ; 2.73 (s, 3H, SMe), 6.97 (s, 1H, 5-H), 7.24 (dd, 1H, 4'-H, J=3.0, 5.0 Hz), 7.86 (d, 1H, 5'-H, J=5.0 Hz), 7.98 (d, 1H, 3'-H, J=3.5 Hz)[4].

6-(2-Benzothienyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3s). This compound (1.26 g, 4.2 mmoles) was obtained in 84% yield from **1a** (1.02 g, 5.0 mmoles) and **2s** (0.88 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give orange leaflets, mp 287-289°; ir(potassium bromide) υ_{max} cm^{-1}: 2205 (CN), 1710 (C=O), 1640, 1580, 1510, 1470, 1340, 1170; uv(ethanol) λ_{max} nm(log ε): 205 nm (4.37), 269 nm (4.01), 408 nm (4.40); ^{1}H-nmr(deuteriochloroform) δ: 2.73 (s, 3H, SMe), 6.58 (s, 1H, 5-H), 7.45-7.50 (m, 2H, benzothienyl 5', 6'-H, J=1.6, 6.6 Hz), 7.85-7.91 (m, 2H, benzothienyl 4', 7'-H, J=1.6, 8.5 Hz), 8.08 (s, 1H, benzothienyl 3'-H); ms *m/z*: 300 (M^++1, 23), 299 (M^+, 100), 272 (11), 271 (47), 228 (16), 196 (13), 161 (35), 133 (15), 89 (25), 55 (10), 44 (28), 43 (10). *Anal*. Calcd. for $C_{15}H_9NO_2S_2$: C, 60.18; H, 3.03; N, 4.68. Found: C, 59.25; H, 2.88; N, 4.71.

6-(2-Furyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3t). This compound (0.35 g, 1.5 mmoles) was obtained in 30% yield from **1a** (1.02 g, 5.0 mmoles) and **2t** (0.55 g, 5.0 mmoles) in a manne similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 200-202°; ir(potassium bromide) υ_{max} cm^{-1}: 3450, 2370, 2340, 2210 (CN), 1720 (C=O), 1620, 1540, 1480, 1460, 1420, 1320, 1250, 1175, 1095, 1005; uv(ethanol) λ_{max} nm(log ε): 220 nm (4.11), 261 nm (4.25), 344 nm (4.36), 395 nm (4.42); ^{1}H-nmr (deuteriochloroform) δ: 2.70 (s, 3H, SMe), 6.65 (d, 1H, furyl 3'-H, J=0.8 Hz), 6.66 (s, 1H, 5-H), 7.26 (m, 1H, fury 4'-H), 7.64 (d, 1H, furyl 5'-H, J=1.9 Hz); ms m/z: 234 (M^++1, 14), 233 (M^+, 100), 205 (45), 162 (27), 95 (72), 75 (10), 45 (5). *Anal*. Calcd.for $C_{11}H_7NO_3S$: C, 56.65; H, 3.03; N, 6.01. Found: C, 56.78; H, 3.14; N, 6.06.

6-[2-(5-Methylfuryl)]-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (3u). This compound (0.54 g, 2.2 mmoles) was obtained in 44% yield from **1a** (1.02 g, 5.0 mmoles) and **2u** (0.62 g, 5.0 mmoles) in a manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 206-207°; ir (potassium bromide) υ_{max} cm^{-1}: 3450, 2220 (CN), 1710 (C=O), 1600, 1570, 1520, 1470, 1380, 1360, 1220, 1190, 1090, 1030, 1000; uv(ethanol) λ_{max}nm(log ε): 225 nm (4.03), 265 nm (4.08), 349 nm (4.22), 405 nm (4.47); ^{1}H-nmr (deuteriochloroform) δ: 2.44 (s, 3H, furyl-Me), 2.69 (s, 3H, SMe), 6.26 (d, 1H, furyl 3'-H, J=3.5 Hz), 6.55 (s, 1H, 5-H), 7.16 (d, 1H, fury 4'-H, J=3.5 Hz); ms m/z:249 (M^++2, 7), 248 (M^++1, 15), 247 (M^+, 100), 220 (6), 219 (42), 176 (34), 144 (9), 109 (22),53 (5). *Anal*. Calcd.for $C_{12}H_9NO_3S$: C, 58.29; H, 3.67; N, 5.66. Found: C, 58.63; H, 3.74; N, 5.85.

4-Methylthio-2-oxo-6-styryl-2*H*-pyran-3-carbonitrile (5a). This compound was prepared by the previous method in 35% yield, mp 221°; ^{1}H-nmr (deuteriochloroform) δ: 2.64 (s, 3H, SMe), 6.24 (s, 1H, 5-H), 6.28 (d, 1H, =CH, J=16.0 Hz), 7.70 (d, 1H, =CH, J=16.0 Hz), 7.24-7.56 (m, 5H, phenyl-H)[4].

6-[(4-Methoxyphenyl)vinyl]-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (5b). This compound was prepared by the previous method in 43% yield, mp 255°; ^{1}H-nmr (deuteriochloroform) δ: 2.68 (s, 3H, SMe), 6.76 (s, 1H, 5-H), 6.92 (d, 1H, =CH, J=16.0 Hz), 6.96 (d, 2H, 3', 5'-H, J=8.0 Hz), 7.52 (d, 1H, =CH, J=16.0 Hz), 7.64 (d, 1H, 2', 6'-H, J=8.0 Hz)[4].

6-[2-(4-*N*,*N*-dimethylaminophenyl)vinyl]-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (5c). A mixture of 1.89 g (10 mmoles) of **4c**, 2.03 g (10 mmoles) of **1a**, 0.8 g (20 mmoles) powdered sodium hydroxide, and 40 ml of DMSO was stirred at room temperature for 1 hour. The reaction mixture was poured into 500 ml of ice-water and the whole was stirred at room temperature for 2 hours. The brown precipitates that appeared were collected by filtration, washed with water, and recrystallized from a mixture of dichloromethane and methanol to give 0.999 g (3.2 mmoles, 32% yield) of black violet leaflets, mp 280-284°; ir(potassium bromide) υ_{max} cm^{-1}: 2202 (CN), 1705 (C=O), 1595, 1560, 1465, 1360, 1162; uv(ethanol) λ_{max}nm (log ε): 253 nm (4.19), 309 nm (4.29), 374 nm (3.67), 397 nm (3.64), 513 nm (4.67); ^{1}H-nmr (deuteriochloroform) δ: 2.65 (s, 3H, SMe), 3.10 (s, 6H, 2xNMe$_2$), 6.12 (s, 1H, 5-H), 6.44 (d, 1H, =CH, J=15.7 Hz), 6.72 (d, 2H, 3', 5'-H, J=9.1 Hz), 7.48 (d, 2H, 2', 6'-H, J=9.1 Hz), 7.68 (d, 2H, =CH, J=15.7 Hz) ; ms *m/z*: 312 (M$^+$, 100), 284 (6), 241 (5), 209 (15), 174 (16), 44 (35). *Anal.* Calcd for $C_{17}H_{16}N_2O_2S$: C, 65.36; H, 5.16; N, 8.97. Found. C, 65.19; H, 5.14; N, 8.88.

6-[2-(4-*N*,*N*-diethylamino)vinyl]-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (5d). A mixture of 2.17 g (10 mmoles) of **4d**, 2.03 g (10 mmoles) of **1a**, 0.80 g (20 mmoles) powdered sodium hydroxide, and 40 ml of DMSO was stirred at room temperature for 1 hour. The reaction mixture was poured into 500 ml of ice-water and the whole was stirred at room temperature for 10 hours. The brown oil that appeared was collected and crystallized by the treatment with methanol to give 0.89 g (2.6 mmoles, 26% yield) of black solids. An analytical sample was recrystallized from a mixture of dichloromethane and methanol to give black violet leaflets, mp 242-246°; ir (potassium bromide) υ_{max} cm^{-1}: 2202 (CN), 1700 (C=O), 1590, 1560, 1460, 1180; uv(ethanol) λ_{max}nm (log ε):252 nm (4.09), 315 nm (4.25), 374 nm (3.52), 397 nm (3.42), 529 nm (4.69);^{1}H-nmr (deuteriochloroform) δ: 1.21 (t, 6H, N-CH$_2$-*CH$_3$*, J=7.1 Hz), 2.61 (s, 3H, SMe), 3.43 (q, 4H, N-CH$_2$-, J=7.1 Hz), 6.07 (s, 1H, 5-H), 6.37 (d, 1H, =CH, J=15.7 Hz), 6.65 (d, 2H, 3', 5'-H, J=9.1 Hz,), 7.42 (d 2H, 2', 6'-H, J=9.1 Hz), 7.63 (d, 1H, =CH, J=15.7 Hz,); ms *m/z*: 340 (M$^+$, 76), 325 (100), 297 (3), 158 (6).

Anal. Calcd for $C_{19}H_{20}N_2O_2S$: C, 67.03; H, 5.92; N, 8.23. Found. C, 66.89; H, 5.96; N, 8.20.

6-[2-(4-*N*,*N*-diphenylamino)vinyl]-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile (5e). A mixture of 3.13 g (10 mmoles) of **4e**, 2.03 g (10 mmoles) of **1a**, 0.80 g (20 mmoles) powdered sodium hydroxide, and 40 ml of DMSO was stirred at room temperature for 1 hour. The reaction mixture was poured into 500 ml of ice-water and the whole was stirred at room temperature for 2 hours. The brown precipitates that appeared were collected by filtration, washed with water, and recrystallized from a mixture of dichloromethane and methanol to give 1.26 g (2.9 mmoles, 29% yield) of red brown leaflets, mp 212-216°; ir (potassium bromide) ν cm^{-1}: 2205 (CN), 1720 (C=O), 1590, 1565, 1494, 1460, 1330, 1280; uv(ethanol) λ_{max}nm (log ε): 305 nm (4.48), 502 nm (4.19); ^{1}H-nmr (deuteriochloroform) δ: 2.62 (s, 3H, SMe), 6.18 (s, 1H, 5-H), 6.48 (d, 1H, =CH, J=15.1 Hz), 6.99 (d, 2H, 3', 5'-H, J=8.8 Hz), 7.14 (d, 2H, 2', 6'-H, J=7.7 Hz), 6.60-7.56 (m, 10H, phenyl-H), 7.61 (d, 1H, =CH, J=15.1 Hz); ms *m/z*: 437 (M$^+$+1, 12), 436 (M$^+$, 38), 313 (8), 298 (7), 53 (33), 42 (100). *Anal.* Calcd for $C_{27}H_{20}N_2O_2S$: C, 74.29; H, 4.62; N, 6.42. Found. C, 74.22; H, 4.71; N, 6.43.

4-Methylthio-2-oxo-6-phenyl-2*H*-pyran-5-carbonitrile (7). A mixture of 0.73 g (5.0 mmoles) of benzoylacetonitrile, 1.02 g (5.0 mmoles) of **1a**, 0.40 g (10 mmoles) powdered sodium hydroxide, and 20 ml of DMSO was stirred at room temperature for 1 hour. The reaction mixture was poured into 300 ml of ice-water and the whole was stirred at room temperature for 1 hour. The brown precipitates that appeared were collected by filtration. A solution of this product and 10 ml of 10% hydrochloric acid in 50 ml methanol was refluxed for 2 hours. After reaction, the solvent was removed by evaporation with rotary evaporator to give brown solid. This product was washed with water, and recrystallized from methanol to give 0.15 g (0.60 mmol, 12%) as yellow leaflets, mp 239-241°; ir (potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1740 (C=O), 1590, 1570, 1520, 1490, 1445, 1360, 1325, 1205, 1130, 1080, 1050, 1030, 1000; uv(ethanol) λ_{max}nm (log ε): 266 nm (4.58), 296 nm (4.23); ^{1}H-nmr (deuteriodimethylsulfoxide) δ: 2.55 (s, 3H, SMe), 5.94 (s, 1H, 3-H), 7.52-7.62 (m, 1H, 3', 4' and 5'-H), 8.24 (d, 2H, 2', 6'-H, J=6.9 Hz); ms *m/z*: 244 (M$^+$+1, 11), 243 (M$^+$, 71), 216 (15), 215 (100), 214 (10), 105 (60), 85 (13), 83 (11), 77 (65), 71 (18), 69 (15), 57 (31), 55 (19), 51 (24), 43 (25). *Anal.* Calcd. for $C_{13}H_9NO_2S$: C, 64.18; H, 3.73; N, 5.76. Found: C, 64.05; H, 3.78; N, 5.83.

Methyl 4-Methylthio-2-oxo-6-phenyl-2*H*-pyran-3-carboxylic acid methylate (8a). This compound was prepared by the previous method in 32% yield, mp 186°; ^{1}H-nmr (deuteriochloroform) δ: 2.78 (s, 3H, SMe), 4.13 (s, 3H, OMe), 7.40 (s, 1H, 5-H), 7.59-7.77 (m, 1H, 3', 4', 5'-H), 7.95-8.04 (m, 2H, 2', 6'-H) [4].

Methyl 6-(4-Methoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carboxylate (8d). This compound was prepared by the previous method in 39% yield, mp 181°; ^{1}H-nmr (deuteriochloroform) δ; 2.79 (s, 3H, SMe), 4.04 (s, 3H, OMe), 4.19 (s, 3H, OMe), 7.23 (d, 2H, 3', 5'-H, J=10.0 Hz), 7.41 (s, 1H, 5-H), 8.11 (d, 2H, 2', 6'-H, J=10.0 Hz) [4].

4-Methylthio-6-phenyl-3-phenylsulfonyl-2*H*-pyran-2-one (9a). A mixture of 0.60 g (5.0 mmoles) of acetophenone (**2a**), 1.27 g (10.0 mmoles) of **1c**, 0.40 g (10 mmoles) powdered sodium hydroxide, and 20 ml of DMSO was stirred at room temperature for 2 hours. The reaction mixture was poured into 300 ml of ice-water and was acidified with 10% hydrochloric acid. The brown precipitates that appeared were collected by filtration, washed with water, and recrystallized from methanol to give a mixture of **9a** and 4-methylthio-6-phenyl-3-phenylsulfonyl-2*H*-2-one (**10a**). These products were separated by recrystallization from toluene and methanol. Compound **9a** was easily dissolved with toluene to give 0.967 g (2.70 mmoles, 54 %) of yellow cotton needles, mp 221-225°; ir (potassium bromide) ν cm^{-1}: 1715 (C=O), 1605, 1570, 1490, 1450, 1310, 1215, 1150, 1085, 1060;^{1}H-nmr (deuteriochloroform) δ: 2.62 (s, 3H, SMe), 6.76 (s, 1H, 5-H), 7.45-7.55 (m, 5H, phenyl-H), 7.62 (dd, 1H, 4"-H, J=6.9, 7.5 Hz), 7.81 (d, 2H, 2', 6'-H, J=7.2 Hz), 8.72 (d, 2H, 2", 6"-H, J=7.2 Hz); ms *m/z*: 358 (M$^+$, 6), 330 (10), 294 (31), 293 (71), 161 (18), 146 (11), 105 (94), 78 (14), 77

(100), 52 (26), 44 (7). *Anal.* Calcd. for $C_{18}H_{14}O_4S_2$: C, 60.32; H, 3.94. Found: C, 60.16; H, 3.77.

6-(4-Methoxyphenyl)-4-methylthio-3-tolylsulfonyl-2*H*-pyran-2-one (9b). A mixture of 0.75 g (5.0 mmoles) of 4-methoxyacetophenone (**2d**), 1.50 g (10.0 mmoles) of **1d**, 0.40 g (10 mmoles) powdered sodium hydroxide, and 20 ml of DMSO was stirred at room temperature for 2 hours. The reaction mixture was poured into 300 ml of ice-water and was acidified with 10% hydrochloric acid. The brown precipitates that appeared were collected by filtration, washed with water, and recrystallized from methanol to give a mixture of **9b** and 6-(4-methoxyphenyl)-4-methylthio-3-tolylsulfonyl-1*H*-pyridin-2one (**10b**). These products were separated by recrystallization from toluene and methanol. Compound **9b** was easily dissolved with toluene to give 1.12 g (2.8 mmoles, 56%) of yellow cotton needles, mp 220-221°; ir (potassium bromide) ν cm^{-1}: 1720 (C=O), 1610, 1580, 1520, 1465, 1430, 1320, 1310, 1275, 1225, 1200, 1190, 1160, 1095, 1075, 1020; ^{1}H-nmr (deuteriochloroform) δ: 2.42 (s, 3H, Me), 2.60 (s, 3H, SMe), 3.88 (s, 3H, OMe), 6.64 (s, 1H, 5-H), 6.97 (d, 2H, 3", 5"-H, J=8.8 Hz), 7.31 (d, 2H, 3', 5'-H, J=8.0 Hz), 7.72 (d, 2H, 2", 6"-H, J=8.8 Hz), 8.04 (d, 2H, 2', 6'-H, J=8.0 Hz); ms *m/z*: 403 (M^++1, 9), 402 (M^+, 33), 374 (32), 368 (10), 339 (12), 338 (38), 337 (100), 291 (10), 235 (10), 191 (15), 135 (73), 92 (12), 91 (19), 83 (10), 77 (15), 73 (11), 71 (11), 69 (13), 60 (12), 57 (19), 55 (17), 45 (38), 44 (69), 43 (22). *Anal.* Calcd. for $C_{20}H_{18}O_5S_2$: C, 59.68; H, 4.51. Found: C, 60.28; H, 4.53.

4-*N*,*N*-Dimethylamino-2-oxo-6-phenyl-2*H*-pyran-3-carbonitrile (12a). ***Method* A**: A solution of 1.22 g (5 mmoles) of **3a**, 1.26 g (10 mmoles) of 50% dimethylamine solution in 100 ml of methanol was refluxed for 5 hours. After reaction, the solvent was evaporated in the rotary evaporator and the resulting residue was crystallized from methanol to give 0.56 g (2.35 mmoles) of pale yellow product in 47% yield. This compound was recrystallized from to give pale yellow needles (**12a**), mp 243-246°, in 21% yield [4].

Method B: A mixture of 1.22 g (5.0 mmoles) of **3a** and 3 ml of 50% dimethylamine solution was heated at 100°C for 10 minutes. After cooling, the reaction mixture was treated with 10 ml of methanol. The precipitate that appeared was collected by filtration to give 0.68 g (1.5 mmoles, 29%) of yellow crystals (**12a**). The solvent of filtration was evaporated in the rotary evaporator to give the yellow residue. The crude product was purified by silica gel chromatography. Elution with hexane-toluene gave 0.59 g (2.4 mmoles, 48% yield) of pale yellow crystlas (**13a**). This compound was recrystallized from methanol to give yellow prisms, mp 99-101°.

2-Oxo-6-phenyl-4-pyrrolidino-2*H*-pyran-3-carbonitrile (12b). ***Method B***: A mixture of **3a** (1.22 g, 5.0 mmoles) and pyrrolidine (20 mmoles) was heated at 150-200°; after reaction, the reaction mixture was cooled, and then crystallized with 20 ml of methanol. The crystallized product that appeared was collected by filtration to give 0.69 g (2.6 mmoles, 52%) of **12b**. This filtrate included by-product of **13b**. An analytical sample was recrystallized from methanol to give colorless needles, mp 287-289°; ir(potassium bromide) υ_{max} cm^{-1}: 2200 (CN), 1685 (C=O), 1630, 1580, 1540, 1460, 1350, 1240, 1160, 1020; uv(ethanol) λ_{max}nm (log ε): 224 nm (4.26), 228 nm (4.27), 248 nm (4.47), 308 nm (4.36); ^{1}H-nmr (deuteriochloroform) δ: 2.09 (br, 4H, N-CH_2-CH_2-), 3.69 (br, 2H, N-CH_2-), 4.12 (br, 2H, N-CH_2-), 6.35 (s, 1H, 5-H), 7.47 (m, 3H, 3', 4' and 5'-H), 7.79 (m, 2H, 2', 6'-H); ms *m/z*: 266 (M^+, 12), 243 (40), 215 (24), 105 (45), 77 (38), 57 (28), 55 (20), 44 (100). *Anal.* Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.17; H, 5.30; N, 10.52. Found: C, 72.22; H, 5.43; N, 10.17.

4-Morpholino-2-oxo-6-phenyl-2*H*-pyran-3-carbonitrile (12c). This compound was prepared by Method A in 48% yield, mp 221°; ir(potassium bromide) υ_{max} cm^{-1}: 2180 (CN), 1690 (C=O). *Anal.* Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92. Found: C, 68.03; H, 4.90; N, 9.98[4].

4-*N*,*N*-Dimethylamino-6-(3-methoxyphenyl)-2-oxo-2*H*-pyran-3-carbonitrile (12d). ***Method B*:** A mixture of **3c** (1.37 g, 5.0 mmoles) and 3 ml of 50% dimethylamine solution was heated at 150-200°; After reaction, the reaction mixture was cooled, and then crystallized with 20 ml of methanol. The crystallized product that appeared was collected by filtration to give 0.54 g (2.0 mmoles, 40%) of **12d**. This filtrate included by-product of **15d**. An analytical sample was recrystallized from methanol to give colorless cotton needles, mp 198-199°; ir (potassium bromide) υ_{max} cm^{-1}: 2200 (CN), 1690 (C=O), 1640, 1590, 1560, 1495, 1470, 1415, 1270, 1235, 1205, 1170, 1120, 1060, 1035, 1005; uv(ethanol) λ_{max}nm (log ε): 220 nm (4.45), 241 nm (4.42), 309 nm (4.27), 324 nm (4.25); ^{1}H-nmr (deuteriochloroform) δ: 3.45 (s, 6H, NMe_2), 3.87 (s, 3H, OMe), 6.41 (s, 1H, 5-H), 7.03-7.07 (m, 1H, 5'-H), 7.33 (m, 1H, 2'-H), 7.36 (m, 2H, 4', 6'-H); ms *m/z*: 271 (M^++1, 14), 270 (M^+, 76), 242 (12), 163 (10), 135 (25), 92 (13), 77 (16), 44 (19), 43 (10). *Anal.* Calcd. for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.39. Found: C, 66.61; H, 5.29; N, 10.26.

6-(4-Methoxyphenyl)-4-*N*,*N*-dimethylamino-2-oxo-2*H*-pyran-3-carbonitrile (12e). This compound (0.675 g, 2.5 mmoles) was obtained in 50% yield from 3d (1.37 g, 5 mmoles) and 3 ml of 50% dimethylamine solution in a manner similar to that described for the synthesis of 12b (Method B). An analytical sample was recrystallized from methanol to give greenish yellow needles, mp 194-196°; ir (potassium bromide) υ_{max} cm^{-1}: 2330, 2200 (CN), 1685 (C=O), 1635, 1605, 1550, 1510, 1460, 1420, 1360, 1300, 1260, 1190, 1130, 1050, 1020; uv(ethanol) λ_{max}nm (log ε): 233 nm (443), 332 nm (4.42); ^{1}H-nmr (deuteriochloroform) δ: 3.43 (s, 6H, NMe_2), 3.87 (s, 3H, OMe), 6.30 (s, 1H, 5-H), 6.96 (d, 2H, 3', 5'-H, J=8.8 Hz), 7.77 (dd, 2H, 2', 6'-H, J= 8.8 Hz); ms *m/z*: 271 (M^++1, 13), 270 (M^+, 70), 266 (11), 256 (10), 242 (14), 136 (11), 135 (100), 121 (11), 107 (10), 97 (13), 95 (10), 92 (11), 91 (10), 85 (11), 84 (119, 83 (17), 81 (14), 77 (15), 73 (12), 71 (18), 70 (11), 69 (29), 67 (10), 60 (15), 57 (32), 56 (12), 55 (31), 45 (27), 44 (87). *Anal.* Calcd. for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.26; H, 5.22; N, 10.16.

6-(4-Methoxyphenyl)-2-oxo-4-pyrrolidino-2*H*-pyran-3-carbonitrile (12f). This compound (0.76 g, 2.55 mmoles) was obtained in 51% yield from **3d** (1.37 g, 5 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **12b** (**Method B**). An analytical sample was recrystallized from methanol to give colorless leaflets, mp 259-260°; ir (potassium bromide) υ_{max} cm^{-1}: 2200 (CN), 1685 (C=O), 1640, 1605, 1540, 1510, 1450, 1420, 1350, 1310, 1250, 1180, 1130, 1060, 1030; uv(ethanol) λ_{max}nm (log ε): 233 nm (4.33), 331 nm (4.41); ^{1}H-nmr (deuteriochloroform) δ: 2.07 (br, 4H, N-CH_2-CH_2-), 3.67 (br, 2H, N-CH_2-), 3.87 (s, 3H, OMe), 4.11 (br, 2H, N-CH_2-), 6.23 (s, 1H, 5-H), 6.95 (d, 2H, 3', 5'-H, J=9.1 Hz), 7.76 (d, 2H, 2', 6'-H, J=9.1 Hz); ms *m/z*: 297 (M^++1, 19), 296 (M^+, 93), 268 (29), 178 (23), 135 (74), 77 (20), 69 (41), 57 (23), 55 (24), 44 (100). *Anal.* Calcd. for $C_{17}H_{16}N_2O_3$: C, 68.91;H, 5.44; N, 9.45. Found: C, 69.03;H, 5.57;N, 9.46.

6-(4-Methoxyphenyl)-4-morpholino-2-oxo-2*H*-pyran-3-carbonitrile (12g). This compound was prepared by **Method A**

in 42% yield, mp 273°; ir(potassium bromide) υ_{max} cm^{-1}: 2180 (CN), 1680 (C=O). *Anal.* Calcd. for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16; N, 8.97. Found: C, 65.25; H, 5.00; N, 8.64 [4].

6-(4-Methoxyphenyl)-2-oxo-4-thiomorpholino-2*H*-pyran-3-carbonitrile (12h). This compound (0.84 g, 2.55 mmoles) was obtained in 51% yield from **3d** (1.37 g, 5.0 mmoles) in manner similar to that described for the preparation of **12b** (**Method B**). An analytical sample was recrystallized from methanol to give colorless leaflets, mp 218-220°; ir (potassium bromide) υ_{max} cm^{-1}: 2900, 2200 (CN), 1720 (C=O), 1620, 1605, 1570, 1510, 1460, 1360, 1310, 1260, 1250, 1180, 1120, 1060, 1020; uv(ethanol) λ_{max}nm (log ε): 236 nm (4.41), 339 nm (4.47); ^{1}H-nmr (deuteriochloroform) δ: 2.87 (nt, 4H, S-CH_2-, J=5.0 Hz), 3.88 (s, 3H, OMe), 4.13 (nt, 4H, N-CH_2-, J=5.0 Hz), 6.33 (s, 1H, 5-H), 6.97 (d, 2H, 3', 5'-H, J=8.8 Hz), 7.77 (d, 2H, 2', 6'-H, J=8.8 Hz); ms *m/z*: 330 (M^++2, 7), 329 (M^++1, 21), 328 (M^+, 100), 327 (10), 255 (24), 254 (13), 226 (16), 135 (89). *Anal.* Calcd. for $C_{17}H_{16}N_2O_3S$: C, 62.18; H, 4.91; N, 8.53. Found: C, 62.17; H, 4.97; N, 8.51.

6-(4-Methoxyphenyl)-2-oxo-4-phenethylamino-2*H*-pyran-3-carbonitrile (12i). This compound was prepared by Method A in 60% yield, mp 224°; ir (potassium bromide) υ_{max} cm^{-1}: 3280 (NH), 2200 (CN), 1680 (C=O). *Anal.* Calcd. for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.77; H, 5.23; N, 7.85[4].

6-(2,5-Dimethoxyphenyl)-4-morpholino-2-oxo-2*H*-pyran-3-carbonitrile (12j). This compound (1.33 g, 3.9 mmoles) was obtained in 78% yield from **3f** (1.52 g, 5.0 mmoles) and 2 ml of morpholine in a manner similar to that described for the preparation of **12a** (**Method A**). An analytical sample was recrystallized from methanol to give yellow leaflets, mp 185-187°; ir (potassium bromide) υ_{max} cm^{-1}: 2930, 2190 (CN), 1690 (C=O), 1620, 1535, 1500, 1465, 1440, 1400, 1310, 1280, 1260, 1240, 1205, 1180, 1060, 1010; uv(ethanol) λ_{max}nm (log ε): 246 nm (4.35), 303 nm (4.22), 364 nm (4.15); ^{1}H-nmr (deuteriochloroform) δ: 3.82 (s, 3H, OMe), 3.87 (br, 8H, morpholino-H), 3.91 (s, 3H, OMe), 6.95 (d, 1H, 4'-H, J=9.1 Hz), 7.04 (dd, 1H, 4'-H, J=3.0, 9.1 Hz), 7.10 (s, 1H, 5-H), 7.44 (d, 1H, 6'-H, J= 3.0 Hz); ms *m/z*: 343 (M^++1, 19), 342 (M^+, 90), 165 (87), 97 (25), 83 (32), 81 (20), 71 (29), 69 (44), 57 (56), 56 (22), 55 (53), 45 (45), 44 (100). *Anal.* Calcd. for $C_{18}H_{18}N_2O_5$: C, 63.15; H, 5.30; N, 8.18. Found: C, 62.55;H, 5.29;N, 7.96.

6-(3,4-Dimethoxyphenyl)-4-morpholino-2-oxo-2*H*-pyran-3-carbonitrile (12k). This compound (1.18 g, 3.45 mmoles) was obtained in 69% yield from **3g** (1.52 g, 5.0 mmoles) and 2ml of morpholine in a manner similar to that described for the preparation of **12a** (**Method A**). An analytical sample was recrystallized from methanol to give greenish yellow leaflets, mp 243-245°; ir (potassiumbromide) υ_{max} cm^{-1}: 2200 (CN), 1690 (C=O), 1625, 1600, 1525, 1510, 1475, 1465, 1445, 1410, 1360, 1280, 1260, 1235, 1210, 1160, 1120, 1060, 1020; uv(ethanol) λ_{max}nm (log ε): 239 nm (4.26), 358 nm (4.25); ^{1}H-nmr (deuteriochloroform) δ: 3.89 (br, 8H, morpholino-H), 3.96 (s, 6H, OMeX2), 6.32 (s, 1H, 5-H), 6.92 (d, 1H, 6'-H, J=8.5 Hz), 7.31 (d, 1H, J=2.2 Hz, 2'-H), 7.40 (dd, 1H, 5'-H, J=2.2, 8.5 Hz); ms *m/z*: 343 (M^++1, 23), 342 (M^+, 98), 165 (98), 97 (26), 85 (25), 83 (28), 71 (32), 69 (34), 57 (55), 55 (39), 45 (100), 43 (42), 41 (30). *Anal.* Calcd. for $C_{18}H_{18}N_2O_5$: C, 63.15; H, 5.30; N, 8.18. Found: C, 63.36; H, 5.33; N, 8.14.

4-*N*,*N*-Dimethylamino-6-(4-dimethylaminophenyl)-2-oxo-2*H*-pyran-3-carbonitrile (12l). This compound (0.91 g, 3.2 mmoles) was obtained in 64% yield **3i** (1.43 g, 5.0 mmoles) and 2 ml of dimethylamine in a manner similar to that described for the preparation of **12b** (**Method B**). An analytical sample was recrystallized from methanol to give yellow needles, mp 265-267°; ir (potassium bromide) υ_{max} cm^{-1}: 2900, 2220 (CN), 1685 (C=O), 1640, 1610, 1550, 1460, 1360, 1210, 1165, 1115, 1060; uv(ethanol) λ_{max}nm (log ε): 237 nm (4.37), 322 nm (3.96), 400 nm (4.57); ^{1}H-nmr (deuteriochloroform) δ: 3.06 (s, 6H, NMe_2), 3.40 (s, 6H, phenyl-NMe_2), 6.20 (s, 1H, 5-H), 6.67 (d, 1H, 3', 5'-H, J=9.1 Hz), 7.70 (d, 2H, 2', 6'-H, J=9.1 Hz); ms *m/z*: 284 (M^++1, 6), 283 (M^+, 25), 148 (32), 97 (11), 83 (14), 73 (13), 71 (14), 69 (19), 60 (12), 57 (28), 56 (10), 55 (27), 44 (100). *Anal.* Calcd. for $C_{16}H_{17}N_3O_2$: C, 67.83; H, 6.05; N, 14.83. Found: C, 67.84; H, 6.12; N, 14.69.

6-(4-*N*,*N*-Dimethylaminophenyl)-4-pyrrolidino-2-oxo-2*H*-pyran-3-carbonitrile (12m). This compound (0.68 g, 2.2 mmoles) was obtained in 44% yield **3i** (1.43 g, 5.0 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **12b** (**Method B**). An analytical sample was recrystallized from methanol to give yellow needles, mp 270-271°; ir (potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1680 (C=O), 1620, 1600, 1515, 1450, 1370, 1340, 1280, 1235, 1200, 1170, 1060, 1015; uv(ethanol) λ_{max}nm (log ε): 237 nm (4.47), 327 nm (4.06), 396 nm (4.64); ^{1}H-nmr (deuteriochloroform) δ: 2.05 (s, 4H, N-CH_2-*CH_2*-), 3.06 (s, 6H, NMe_2), 3.65 (m, 2H, N-CH_2-), 4.08 (m, 2H N-CH_2-), 6.13 (s, 1H, 5-H), 6.67 (d, 2H, 3', 5'-H, J=9.1 Hz), 7.70 (d, 2H, 2', 6'- H, J=9.1 Hz); ms *m/z*: 310 (M^++1, 10), 309 (M^+, 45), 256 (11), 178 (10), 148 (29), 129 (10), 97 (13), 95 (11), 92 (10), 91 (28), 84 (10), 83 (17), 82 (10), 81 (14), 77 (13), 73 (14), 71 (13), 70 (11), 69 (27), 67 (14), 60 (12), 57 (25), 56 (10), 55 (32), 45 (12), 44 (100). *Anal.* Calcd. for $C_{18}H_{19}N_3O_2$: C, 63.15; H, 5.30; N, 8.18. Found: C, 62.55; H, 5.29; N, 7.96.

6-(4-*N*,*N*-Dimethylaminophenyl)-4-morpholino-2-oxo-2*H*-pyran-3-carbonitrile (12n). This compound (0.81 g, 2.5 mmoles) was obtained in 50% yield **3i** (1.43 g, 5.0 mmoles) and 2 ml of morpholine in a manner similar to that described for the preparation of **12a** (**Method A**). An analytical sample was recrystallized from methanol to give orange needles, mp 273-275°; ir (potassium bromide) υ_{max} cm^{-1}: 2900, 2850, 2195 (CN), 1680 (C=O), 1590, 1520, 1460, 1360, 1250, 1220, 1200, 1160, 1110, 1060; uv(ethanol) λ_{max}nm (log ε): 240 nm (4.30), 4.09 nm (4.42); ^{1}H-nmr (deuteriochloroform) δ: 3.06 (s, 6H, NMe_2), 3.84 (m, 6H, morpholino-H), 6.21 (s, 1H, 5-H), 6.68 (d, 2H, 3', 5'-H, J=9.1 Hz), 7.70 (d, 2H, 2', 6'-H, J=9.1 Hz); ms *m/z*: 326 (M^++1, 18), 325 (M^+, 82), 286 (34), 149 (12), 148 (100), 105 (10), 77 (10), 57 (12), 55 (11), 44 (23), 43 (12), 42 (13). *Anal.* Calcd. for $C_{18}H_{19}N_3O_3$: C, 66.45; H, 5.89; N, 12.91. Found: C, 66.34; H, 5.84; N, 12.61.

6-(4-*N*,*N*-Dimethylaminophenyl)-4-thiomorpholino-2-oxo-2*H*-pyran-3-carbonitrile (12o). This compound (0.99 g, 2.9 mmoles) was obtained in 58% yield from **3i** (1.43 g, 5.0 mmoles) and 2 ml of thiomorpholine in a manner similar to that described for the preparation of **12a** (**Method A**). An analytical sample was recrystallized from methanol to give orange leaflets, mp 275-277°; ir (potassium bromide) υ_{max} cm^{-1}: 2910, 2200 (CN), 1680 (C=O), 1600, 1520, 1460, 1370, 1300, 1275, 1255, 1220, 1200, 1170, 1120, 1060; uv(ethanol) λ_{max}nm (log ε): 410 nm (4.57); ^{1}H-nmr (deuteriochloroform) δ: 2.83-2.87 (m, 4H, thiomorpholino 2, 5-H), 3.07 (s, 6H, NMe_2), 4.07-4.11 (m, 4H, thiomorpholino 3, 4-H), 6.22 (s, 1H, 5-H), 6.97 (d, 2H, J=9.3 Hz, 3', 5'-H), 7.70 (d, 2H, 2', 6'-H, J=9.3 Hz); ms *m/z*: 341 (M^+, 47), 286 (55), 111 (22), 97 (22), 85 (32), 84 (20), 81 (23), 71 (49), 70 (22), 69 (43), 57 (78), 56 (23), 55 (52), 44(100).

Anal. Calcd. for $C_{18}H_{19}N_3O_2S$: C, 63.32; H, 5.61; N, 12.31. Found: C, 63.25; H, 5.57; N, 12.15.

6-(4-Bromophenyl)-4-pyrrolidino-2-oxo-2*H*-pyran-3-carbonitrile (12p). This compound (0.91 g, 2.65 mmoles) was obtained in 53% yield from **3j** (1.61 g, 5.0 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **12b** (**Method B**). An analytical sample was recrystallized from methanol to give yellow leaflets, mp 282-284°; ir (potassium bromide) υ_{max} cm^{-1}: 3090, 2990, 2210 (CN), 1690 (C=O), 1640, 1590, 1540, 1500, 1470, 1410, 1350, 1260, 1240, 1200, 1100, 1080, 1060, 1010; uv(ethanol) λ_{max}nm (log ε): 231 nm (4.37), 250 nm (4.40), 315 nm (4.42); ^{1}H-nmr (deuteriochloroform) δ: 2.11 (br, 4H, N-CH_2-*CH_2*-), 3.69 (m, 2H, N-CH_2), 4.12 (m, 2H, N-CH_2-), 6.33 (s, 1H, 5-H), 7.59 (d, 2H, 2', 6'-H, J=9.1 Hz), 7.66 (d, 2H, 3', 5'-H, J=9.1 Hz); ms *m/z*: 344 (M^+, 10), 323 (38), 321 (37), 295 (23), 293 (24), 289 (32), 185 (26), 151 (20), 75 (21), 57 (27), 55 (21), 44 (100). *Anal.* Calcd. for $C_{16}H_{13}N_2O_2Br$: C, 55.67; H, 3.80; N, 8.12. Found: C, 56.11; H, 3.92; N, 8.23.

6-(4-Chlorophenyl)-4-pyrrolidino-2-oxo-2*H*-pyran-3-carbonitrile (12q). This compound (0.83 g, 2.75 mmoles) was obtained in 55% yield from **3l** (1.39 g, 5.0 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **12b** (**Method B**). An analytical sample was recrystallized from methanol to give yellow cotton needles, mp 288-290°; ir (potassium bromide) υ_{max} cm^{-1}: 2200 (CN), 1685 (C=O), 1640, 1535, 1495, 1465, 1400, 1345, 1240, 1170, 1090, 1060, 1010; uv(ethanol) λ_{max}nm (log ε): 249 nm (4.41), 314 nm (4.38); ^{1}H-nmr (deuteriochloroform) δ: 2.12 (br, 4H, N-CH_2-*CH_2*-), 3.72 (br, 2H, N-CH_2-), 4.16 (br, 2H, N-CH_2-), 6.33 (s, 1H, 5-H), 7.46 (d, 2H, 2', 6'-H, J=8.5 Hz), 7.76 (d, 2H, 3', 5'-H, J=8.5 Hz); ms *m/z*: 302 (M^++2, 28), 301 (M^++1, 28), 300 (M^+, 75), 271 (22), 141 (23), 139 (61), 133 (20), 111 (36), 98 (20), 97 (37), 95 (25), 85 (32), 84 (20), 83 (38), 81 (28), 71 (46), 70 (43), 69 (49), 68 (26), 67 (27), 57 (70), 56 (23), 55 (57), 44 (100). *Anal.* Calcd. for $C_{16}H_{13}N_2O_2Cl$: C, 63.90; H, 4.36; N, 9.31. Found: C, 64.53; H, 4.59; N, 8.86.

6-(4-Chlorophenyl)-2-oxo-4-pyrrolidino-2*H*-pyran-3-carbonitrile (12r). This compound (1.11 g, 3.7 mmoles) was obtained in 73% yield from **3l** (1.39 g, 5.0 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **12b** (**Method B**). An analytical sample was recrystallized from methanol to give yellow cotton needles, mp 288-290°; ir (potassium bromide) υ_{max} cm^{-1}: 2200 (CN), 1685 (C=O), 1640, 1535, 1495, 1465, 1400, 1345, 1240, 1170, 1090, 1060, 1010; uv(ethanol) λ_{max}nm (log ε): 249 nm (4.41), 314 nm (4.38); ^{1}H-nmr (deuteriochloroform) δ: 2.12 (br, 4H, N-CH_2-*CH_2*-), 3.72 (m, 2H, N-CH_2), 4.16 (m, 2H, N-CH_2-), 6.35 (s, 1H, 5-H), 7.46 (d, 2H, 2', 6'-H, J=8.5 Hz), 7.76 (d, 2H, 3', 5'-H, J=8.5 Hz); ms *m/z*: 302 (M^++2, 28), 301 (M^++1, 28), 300 (M^+, 75), 271 (22), 141 (23), 139 (61), 133 (20), 111 (36), 98 (20), 97 (37), 95 (25), 85 (32), 84 (20), 83 (38), 81 (28), 71 (46), 70 (43), 69 (49), 68 (26), 67 (27), 57 (70), 56 (23), 55 (57), 44 (100). *Anal.* Calcd. for $C_{16}H_{13}N_2O_2Cl$: C, 63.90; H, 4.36; N, 9.31. Found: C, 64.53; H, 4.59; N, 8.86.

6-Biphenyl-2-oxo-4-pyrrolidino-2*H*-pyran-3-carbonitrile (12s). This compound (0.75 g, 2.2 mmoles) was obtained in 44% yield from **3m** (1.60 g, 5.0 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **12a** (**Method A**). An analytical sample was recrystallized from methanol to give colorless cotton needles, mp 304-305°; ir (potassium bromide) υ_{max} cm^{-1}: 3100, 2960, 2220 (CN), 1700 (C=O), 1640, 1540, 1470, 1410, 1350, 1240, 1070, 1010; uv(ethanol) λ_{max} nm (log ε): 328 nm (4.56); ^{1}H-nmr (deuteriochloroform) δ: 2.10 (br, 4H, N-CH_2-*CH_2*-), 3.71 (br, 2H, N-CH_2-), 4.14 (br, 2H, N-CH_2-), 6.39 (s, 1H, 5-H), 7.42-7.49 (m, 1H, 3'', 4'' and 5''-H), 7.61 (d, 2H, 2', 6'-H, J=8.5 Hz), 7.67 (d, 2H, 3', 5'-H, J=8.5 Hz), 7.87 (m, 2H, 2'', 6''-H); ms *m/z*: 343 (M^++1, 22), 342 (M^+, 71), 313 (22), 312 (37), 181 (39), 153 (22), 152 (29), 135 (56), 111 (30), 109 (23), 99 (21), 98 (26), 97 (44), 95 (34), 85 (46), 84 (26), 83 (54), 82 (20), 81 (34), 77 (20), 71 (33), 69 (60), 67 (30), 57 (100), 56 (30), 55 (72), 44 (99). *Anal.* Calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.40; H, 5.44; N, 8.14.

6-(1-Naphthyl)-2-oxo-4-pyrrolidino-2*H*-pyran-3-carbonitrile (12t). This compound (1.36 g, 4.3 mmoles) was obtained in 86% yield from **3o** (1.47g, 5.0 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **12a** (**Method A**). An analytical sample was recrystallized from methanol to give yellow leaflets, mp 259-261°; ir (potassium bromide) υ_{max} cm^{-1}: 2950, 2850, 2200 (CN), 1700 (C=O), 1640, 1530, 1465, 1350, 1260, 1240, 1180, 1110, 1060, 1010; uv(ethanol) λ_{max} nm (log ε): 218 nm (4.87), 320 nm (4.30); ^{1}H-nmr (deuteriochloroform) δ: 2.08 (br, 4H, N-CH_2-*CH_2*-), 3.63 (m, 2H, N-CH_2-), 4.17 (m, 2H, N-CH_2-), 6.25 (s, 1H, 5-H), 7.52 (dd, 1H, naphtyl 3'-H, J=7.2, 8.5 Hz), 7.55-7.59 (m, 2H, naphtyl 6, 7-H), 7.66 (dd, 1H, naphtyl 4'-H, J=1.3, 7.2 Hz), 7.91 (m, 1H, naphtyl 5'-H), 8.06 (d, 1H, naphtyl 2'-H, J=8.5 Hz), 8.13 (m, 1H, naphtyl 8'-H); ms *m/z*: 317 (M^++1, 17), 316 (M^+, 66), 155 (65), 127 (60), 97 (26), 85 (24), 83 (26), 71 (35), 70 (33), 69 (38), 57 (55), 56 (20), 55 (44), 44 (100). *Anal.* Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.85. Found: C, 76.44; H, 5.34; N, 9.03.

4-Morpholino-6-(1-naphthyl)-2-oxo-2*H*-pyran-3-carbonitrile (12u). This compound (1.46 g, 4.4 mmoles) was obtained in 88% yield from **3o** (1.47 g, 5 mmoles) and 2 ml of morpholine in a manner similar to that described for the preparation of **12a** (**Method A**). An analytical sample was recrystallized from methanol to give colorless prisms, 206-208°; ir (potassium bromide) υ_{max} cm^{-1}: 2970, 2925, 2850, 2200 (CN), 1700 (C=O), 1635, 1585, 1530, 1465, 1440, 1390, 1355, 1315, 1260, 1240, 1110, 1065, 1010; uv(ethanol) λ_{max}nm (log ε): 219 nm (4.88), 324 nm (4.33); ^{1}H-nmr (deuteriochloroform) δ: 3.89 (s, 8H, morpholino-H), 6.33 (s, 1H, 5-H), 7.52 (dd, 1H, naphthyl 3-H, J=7.2 ,8.4 Hz), 7.54-7.63 (m, 2H, naphthyl 6', 7'-H), 7.67 (d, 1H, naphthyl 2'-H, J=7.2 Hz), 7.92 (m, 1H, naphthyl 5'-H), 7.99 (d, 1H, naphthyl 4'-H, J=8.4 Hz, 8.10 (m, 1H, naphthyl 8'-H); ms *m/z*: 333 (M^++1, 20), 332 (M^+, 79), 155 (100), 127 (46), 97 (11), 85 (12), 83 (13), 71 (16), 69 (16), 57 (26), 55 (18), 44 (14), 43 (19). *Anal.* Calcd. for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.07; H, 4.92; N, 8.30.

2-Oxo-4pyrrolidino-6-(2-thienyl)-2*H*-pyran-3-carbonitrile (12v). This compound (0.57 g, 2.1 mmoles) was obtained in 42% yield from **3r** (1.09 g, 5.0 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **12a** (**Method A**). An analytical sample was recrystallized from methanol to give greenish yellow needles, mp 283-285°; ir (potassium bromide) υ_{max} cm^{-1}: 3100, 2980, 2200 (CN), 1690 (C=O), 1630, 1540, 1460, 1420, 1380, 1360, 1330, 1250, 1065, 1030, 1000; uv(ethanol) λ_{max}nm (log ε): 253 nm (4.31), 331 nm (4.36), 336 nm (4.36); ^{1}H-nmr (deuteriochloroform) δ: 2.08 (br, 4H, N-CH_2-*CH_2*-), 3.66 (m, 2H, N-CH_2-), 4.11 (m, 2H, N-CH_2-), 6.18 (s, 1H, 5-H), 7.13 (dd, 1H, thienyl 4'-H, J=3.8, 4.9 Hz), 7.51 (dd, 1H, thienyl 5'-H, J= 1.1, 4.9 Hz), 7.66 (dd, 1H, thienyl

3'-H, J=1.1, 3.8 Hz); ms *m/z*: 273 (M^++1, 18), 272 (M^+, 100), 271 (10), 244 (27), 243 (19), 239 (19), 239 (16), 227 (13), 216 (12), 215 (14), 211 (20), 161 (10), 147 (11), 111 (91), 94 (12), 83 (12), 71 (13), 70 (38), 69 (14), 68 (10), 57 (19), 44 (28), 43 (19). *Anal*. Calcd. for $C_{14}H_{12}N_2O_2S$: C, 61.75; H, 4.44; N, 10.29. Found: C, 61.52; H, 4.46; N, 10.29.

4-Morpholino-2-oxo-6-(2-thienyl)-2*H*-pyran-3-carbonitrile (12w). This compound (0.68 g, 2.35 mmoles) was obtained in 47% yield from **3r** (1.09 g, 5.0 mmoles) and 2 ml of morpholine in a manner similar to that described for the preparation of **12a** (**Method A**). An analytical sample was recrystallized from methanol to give yellow leaflets, mp 249-250°; ir (potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1700 (C=O), 1620, 1530, 1470, 1375, 1305, 1250, 1115, 1060, 1030; uv(ethanol) λ_{max}nm (log ε): 255 nm (4.27), 343 nm (4.57); ^{1}H-nmr (deuteriochloroform) δ: 3.88 (br, 8H, morpholino-H), 6.26 (s, 1H, 5-H), 7.16 (dd, 1H, thienyl 4'-H, J=3.8, 4.9 Hz), 7.56 (dd, 1H, thienyl 5'-H, J=1.1, 4.9 Hz), 7.70 (dd, 1H, thienyl 3'-H, J=1.1, 3.8 Hz); ms *m/z*: 289 (M^++1, 11), 288 (M^+, 55), 111 (64), 97 (24), 83 (21), 71 (25), 69 (44), 57 (55), 56 (26), 55 (61), 45 (20), 44 (100). *Anal*. Calcd. for $C_{14}H_{12}N_2O_3S$: C, 58.32; H, 4.20; N, 9.72. Found: C, 58.39; H, 4.14; N, 9.67.

6-(2-Benzothienyl)-2-oxo-4-piperidino-2*H*-pyran-3-carbonitrile (12x). This compound (0.89 g, 2.65 mmoles) was obtained in 53% yield from **3s** (1.34 g, 5 mmoles) and 2 ml of piperidine in a manner similar to that described for the preparation of **12a** (**Method A**). An analytical sample was recrystallized from methanol to give yellow leaflets, mp 247-248°; ir (potassium bromide) υ_{max} cm^{-1}: 2920, 2850, 2200 (CN), 1710 (C=O), 1620, 1540, 1450, 1360, 1310, 1230, 1190, 1175, 1070, 1020; uv(ethanol) λ_{max}nm (log ε): 217 nm (4.52), 240 nm (4.35), 256 nm (4.25), 349 nm (4.45); ^{1}H-nmr (deuteriochloroform) δ: 1.82 (br, 6H, piperidino 3, 4, 5-H), 3.83 (m, 4H, N-CH_2-), 6.35 (s, 1H, 5-H), 7.41-7.46 (m, 2H, benzothienyl 5', 6'-H), 7.81-7.86 (m, 2H, benzothienyl 4', 7'-H), 7.97 (s, 1H, benzothienyl 3'-H); ms *m/z*: 337 (M^++1, 20), 336 (M^+, 91), 303 (26), 236 (23), 161 (58), 111 (23), 98 (22), 97 (44), 96 (25), 95 (25), 85 (32), 84 (38), 83 (58), 82 (30), 71 (49), 70 (27), 69 (71), 68 (21), 67 (29), 60 (15), 58 (10), 57 (100), 56 (29), 55 (84), 54(16), 45(14), 44 (69), 43 (86). *Anal*. Calcd. for $C_{19}H_{16}N_2O_2S$: C, 67.84; H, 4.79; N, 8.33. Found: C, 68.27; H, 4.85; N, 8.29.

Methyl 4-Methylamino-2-oxo-6-phenyl-2*H*-pyran-3-carboxylate (14a). A solution of 0.58 g (2.0 mmoles) of **13a** and 2ml of 40% methylamine-water solution in 50 ml of methanol was refluxed for 3 hours. After removal of the solvent, the residue was recrystallized from methanol to give 0.49 g (1.9 mmoles, 95% yield) of colorless needles, mp 162-165°; ir (potassium bromide) ν_{max} cm^{-1}; 3220 (NH), 1715 (C=O), 1650, 1565; uv(ethanol) λ_{max}nm(log ε): 240 nm (4.52), 315 nm (4.38); ^{1}H-nmr (deuteriochloroform) δ: 3.12 (d, 3H, NMe, J=4.9 Hz), 3.89 (s, 3H, OMe), 6.46 (s, 1H, 5-H), 7.40-7.52 (m, 3H, phenyl-H), 7.80-7.91 (m, 2H, phenyl-H), 10.00 (br, 1H, NH); ms *m/z*: 259 (M^+, 16), 246 (16), 245 (100), 215 (46), 188 (30),147 (15), 105 (53), 77 (30). *Anal*. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.49, H, 4.88; N, 5.33.

Methyl 4-Benzylamino-2-oxo-6-phenyl-2*H*-pyran-3-carboxylate (14b). A solution of 0.58 g (2.0 mmoles) of **13a** and 0.27 g(2.5 mmoles) of benzylamine in 50 ml of methanol was refluxed for 30 min. After removal of the solvent, the residue was recrystallized from methanol to give 0.50 g (1.5 mmoles, 75% yield) of colorless needles, mp 197-198°; ir (potassium bromide) ν_{max} cm^{-1}: 3450 (br, NH), 1715 (C=O), 1660 (C=O), 1562, 1275; uv(ethanol)λ_{max} nm(log ε): 241 nm (4.43), 305 nm (4.28); ^{1}H-nmr (deuteriochloroform)δ: 3.90 (s, 3H, OMe), 4.64 (d, 2H, N-CH_2-, J=5.8 Hz), 6.44 (s, 1H, 5-H), 7.32-7.52 (m, 8H, phenyl-H), 7.50-7.80 (m, 2H, phenyl-H), 10.44 (br, 1H, NH); ms *m/z*: 336 (M^++1, 23), 335 (M^+, 100), 303 (60), 245 (100), 274 (34), 230 (31),105 (44), 91 (75), 77 (30). *Anal*. Calcd for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11; N, 4.18. Found: C, 71.37, H, 5.11; N, 4.14.

Methyl 4-*N*,*N*-Dimethylamino-2-oxo-6-phenyl-2*H*-pyran-3-carboxylate (14c). A solution of 0.58 g (2 mmoles) of **14a** and 2ml of 50% methylamine-water solution in 50 ml of methanol was refluxed for 1 hour. After removal of the solvent, the residue was recrystallized from methanol to give 0.54 g (1.96 mmoles, 98% yield) of colorless needles, mp 140-145°; ir (potassium bromide) ν_{max} cm^{-1}: 1720 (C=O), 1635, 1538, 1470; uv(ethanol)λ_{max} nm(log ε): 248 nm (4.47), 303 nm (4.28); ^{1}H-nmr (deuteriochloroform) δ: 3.11 (s, 6H, NMe_2), 3.89 (s, 3H, OMe), 6.47 (s, 1H, 5-H), 7.40-7.52 (m, 3H, phenyl-H), 7.70-7.85 (m, 2H, phenyl-H); ms *m/z*: 273 (M^+, 77), 246 (16), 245 (41), 242 (66), 241 (79), 105 (100), 77 (79), 45 (48). *Anal*. Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53; N, 5.13. Found: C, 65.57, H, 5.39; N, 5.03.

Methyl 4-Methylamino-6-(4-methoxyphenyl)-2-oxo-2*H*-pyran-3-carboxylate (14d). A solution of 0.64 g (2.0 mmoles) of **14b** and 2ml of 40% methylamine-water solution in 50 ml of methanol was refluxed for 3 hours. After removal of the solvent, the residue was recrystallized from methanol to give 0.55 g (1.9 mmoles, 95% yield) of colorless needles, mp 181-186°; ir (potassium bromide) ν_{max} cm^{-1}: 3220 (NH), 1742, 1722 (C=O), 1640, 1560, 1270; uv(ethanol)λ_{max}nm (log ε): 341 nm (4.38); ^{1}H-nmr (deuteriochloroform) δ: 3.11 (d, 3H, N-Me, J=5.1 Hz), 3.88 (s, 3H, OMe), 3.89 (s, 3H, OMe), 6.34 (s, 1H, 5-H), 6.97 (d, 2H, 3', 5'-H, J=8.8 Hz), 7.85 (d, 2H, 2', 6'-H, J=8.8 Hz), 9.96 (br, 1H, NH); ms *m/z*: 289 (M^+, 59), 261 (26), 256 (19), 149 (12), 135 (38),69 (40), 45 (55), 41 (100). *Anal*. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.17, H, 5.11; N, 4.82.

Methyl 4-Dimethylamino-6-(4-methoxyphenyl)-2-oxo-2*H*-pyran-3-carboxylate (14e). A solution of 0.64 g (2.0 mmoles) of **13b** and 2ml of 40% methylamine-water solution in 50 ml of methanol was refluxed for 1 hour. After removal of the solvent, the residue was recrystallized from methanol to give 0.43 g (1.44 mmoles, 72% yield) of colorless needles, mp 150-151°; ir (potassium bromide) υ_{max} cm^{-1}: 1730 (C=O), 1665 (C=O), 1635, 1550; uv(ethanol)λ_{max}nm(log ε): 321 nm (4.41); ^{1}H-nmr (deuteriochloroform) δ: 3.09 (s, 3H, NMe_2), 3.85 (s, 3H, OMe), 3.88 (s, 3H, OMe), 6.36 (s, 1H, 5-H), 6.93 (d, 2H, 3', 5'-H, J=9.1 Hz), 7.77 (d, 2H, 2', 6'-H, J=9.1 Hz); ms *m/z*: 304 (M^++1, 16), 303 (M^+, 75), 275 (33), 272 (34), 135 (89), 43 (100). *Anal*. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.41, H, 5.73; N, 4.62.

Methyl 6-(4-Methoxyphenyl)-4-pyrrolidino-2-oxo-2*H*-pyran-3-ccarboxylate (14f). A solution of 0.64 g (2.0 mmoles) of **13b** and 0.20 g (3.0 mmoles) of pyrrolidine in 50 ml of methanol was refluxed for 3 hours. After removal of the solvent, the residue was recrystallized from methanol to give 0.47 g (1.44 mmole, 72% yield) of colorless needles, mp 185-186°; ir(potassium bromide) υ_{max} cm^{-1}: 1690 (C=O), 1640 (C=O), 1540, 1515, 1255; uv(ethanol)λ_{max}nm (log ε): 313 nm (4.37); ^{1}H-nmr (deuteriochloroform) δ: 1.58 (m, 4H, pyrrolidino-H), 3.48 (m, 4H, pyrrolidino-H), 3.86 (s, 3H, OMe), 3.90 (s, 3H, OMe), 6.31 (s, 1H, 5-H), 6.95 (d, 2H, 3', 5'-H, J=9.1 Hz), 7.77

(d, 2H, 2', 6'-H, J=9.1 Hz); ms *m/z*: 330 (M^++1, 10), 329 (M^+, 51), 298 (42), 297 (80), 185 (29), 135 (100), 69 (62), 44 (87), 43 (84). *Anal.* Calcd for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.81; N, 4.25. Found: C, 65.34, H, 5.79; N, 4.18.

5-Dimethilamino-3-methylthiopenta-5-phenyl-2,4-dienenitirile (15a). This compound (0.59 g, 2.4 mmoles) was obtained in 48% yield from **3a** (1.22 g, 5 mmoles) and 3 ml of 50% of dimethylamine solution in a manner similar to that described for the preparation of **12a** (**Method B**). An analytical sample was recrystallized from methanol to give yellow prisms, mp 99-101°. Ir (potassium bromide) υ_{max} cm^{-1}: 2170 (CN), 1560, 1495, 1460, 1440, 1410, 1365, 1300, 1245, 1215, 1140, 1090, 1020; ^{1}H-nmr (deuteriochloroform) δ: 2.07 (s, 3H, SMe), 2.79 (s, 6H, NMe_2), 4.37 (s, 1H, =CH-CN), 5.50 (s, 1H, =CH), 7.25-7.38 (m, 5H, phenyl-H); ms *m/z*: 245 (M^++1, 10), 244 (M^+, 59), 229 (18), 198 (16), 197 (100), 182 (14), 157 (13), 154 (20), 153 (12), 127 (18), 118 (10), 77 (18), 44 (14). *Anal.* Calcd. for $C_{14}H_{16}N_2S$: C, 68.81; H, 6.60; N, 11.46. Found: C, 68.48; H, 6.69; N, 11.40.

3-Methylthiopenta-5-phenyl-5-pyrrolidino-2,4-dienenitirile (15b). This compound (0.59 g, 2.4 mmoles) was obtained in 48% yield from **3a** (1.22 g, 5.0 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **15a** (**Method B**). An analytical sample was recrystallized from methanol to give pale yellow needles, mp 99-101°; ir (potassium bromide) υ_{max} cm^{-1}: 3100, 2960, 2850, 2180 (CN), 1560, 1490, 1430, 1380, 1290, 1230, 1210, 1180, 1120, 1070, 1020; ^{1}H-nmr (deuteriochloroform) δ: 2.03 (s, 4H, pyrrolidino 3,4-H), 2.05 (s, 3H, SMe), 3.16 (s, 4H, pyrrolidino 2, 5-H), 4.26 (s, 1H, =CH-CN), 5.57 (s, 1H, =CH), 7.27-7.39 (m, 5H, phenyl-H); ms *m/z*: 271 (M^++1, 7), 270 (M^+, 35), 255 (15), 224 (18), 223 (100), 183 (21), 154 (14), 127 (13), 70 (22), 44 (3), 43 (5). *Anal.* Calcd. for $C_{16}H_{18}N_2S$: C, 71.07; H, 6.71; N, 10.36. Found: C, 70.77; H, 6.89; N, 10.29.

5-Dimethylamino-5-(4-methoxyphenyl)-3-methylthiopenta-2,4-dienenitirile (15e). This compound (0.64 g, 2.4 mmoles) was obtained in 47% yield from **3d** (1.37g, 5 mmoles) and 2 ml of 50% of dimethylamine solution in a manner similar to that described for the preparation of **15a** (**Method B**). An analytical sample was recrystallized from methanol to give yellow leaflets, mp 103-105°; ir (potassium bromide) υ_{max} cm^{-1}: 2925, 2180 (CN), 1610, 1560, 1510, 1460, 1440, 1410, 1365, 1295, 1245, 1170, 1090, 1030; ^{1}H-nmr (deuteriochloroform) δ: 2.08 (s, 3H, SMe), 2.79 (s, 6H, NMe_2), 3.85 (s, 3H, OMe), 4.37 (s, 1H, =CH-CN), 5.49 (s, 1H, =CH), 6.89 (d, 2H, 2', 6'-H, J=8.8 Hz), 7.20 (d, 2H, 3', 5'-H, J=8.8 Hz); ms *m/z*: 275 (M^++1, 13), 274 (M^+, 66), 259 (20), 228 (17), 227 (100), 184 (15), 135 (13), 44 (19). *Anal.* Calcd. for $C_{15}H_{18}N_2OS$: C, 65.66; H, 6.61; N, 10.21. Found: C, 66.83; H, 6.74; N, 10.32.

3-Methylthio-5-(4-methoxyphenyl)-penta-5-pyrrolidino-2,4-dienenitirile (15f). This compound (0.45 g, 1.5 mmoles) was obtained in 30% yield from **3d** (1.37g, 5 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **15a** (**Method B**). An analytical sample was recrystallized from methanol to give yellow prisms, 132-134°; ir (potassium bromide) υ_{max} cm^{-1}: 3100, 2950, 2870, 2180 (CN), 1605, 1550, 1510, 1470, 1420, 1370, 1290, 1250, 116 5, 1105, 1030; ^{1}H-nmr (deuteriochloroform) δ: 1.89 (s, 4H, pyrrolidino 3, 4-H), 2.06 (s, 3H, SMe), 3.85 (s, 4H, pyrrolidino 2, 5-H), 4.25 (s, 1H, =CH-CN), 5.56 (s, 1H, =CH), 6.89 (d, 2H, 2', 6'-H J=8.8 Hz), 7.20 (d, 2H, 3', 5'-H, J=8.8 Hz); ^{13}C-nmr (deuteriochloroform) δ: 16.14 (SMe), 25.34 (C2, 3), 49.10 (C1, 4), 55.24 (OMe), 77.98 (C8), 95.29 (C6), 113.57 (C13, 15), 114.53 (CN), 120.32 (C7), 129.74 (C11), 130.82 (C12,16), 154.13 (C5), 160.33 (C14); ms *m/z*: 301 (M^++1, 10), 300 (M^+, 43), 285 (19), 254 (20), 253 (100), 213 (24), 184 (23), 70 (12), 44 (14), 43 (13). *Anal.* Calcd. for $C_{17}H_{20}N_2OS$: C, 67.97; H, 6.71; N, 9.32. Found: C, 68.05; H, 6.66; N, 9.41.

3-Methylthio-5-(4-methoxyphenyl)-penta-5-thiomorpholino-2,4-dienenitirile (15h). This compound (0.37 g, 1.1 mmoles) was obtained in 22% yield from **3d** (1.37g, 5 mmoles) and 2 ml of thiomorpholine in a manner similar to that described for the preparation of **15a** (**Method B**). An analytical sample was recrystallized from methanol to give yellow leaflets, mp 104-106°; ir (potassium bromide) υ_{max} cm^{-1} : 2925, 2200 (CN), 1610, 1565, 1510, 1460, 1440, 1420, 1380, 1350, 1320, 1300, 1290, 1245, 1230, 1200, 1170, 1150, 1140, 1025; ^{1}H-nmr (deuteriochloroform) δ: 2.11 (s, 3H, SMe), 2.62 (m, 4H, thiomorpholino-H), 3.40 (m, 4H, thiomorpholino-H), 3.84 (s, 3H, OMe), 4.48 (s, 1H, =CH-CN), 5.53 (s, 1H, =CH), 6.87 (d, 2H, 2', 6'-H, J=8.8 Hz), 7.24 (d, 2H, 3', 5'-H, J=8.8 Hz); ms *m/z*: 333 (M^++1, 10), 332 (M^+, 44), 317 (10), 286 (21), 285 (100), 245 (7), 184 (13), 183 (8), 140 (8), 134 (8), 87 (13), 45 (8). *Anal.* Calcd. for $C_{17}H_{20}N_2O_2S_2$: C, 61.41; H, 6.06; N, 8.43. Found: C, 60.86; H, 5.95; N, 8.29.

5-Dimethylamino-5-(4-dimethylaminophenyl)-3-methylthiopenta-2,4-dienenitirile (15l). This compound (0.55g, 1.9 mmoles) was obtained in 38% yield from **3i** (1.43g, 5 mmoles) and 2 ml of 50% of dimethylamine solution in a manner similar to that described for the preparation of **15a** (**Method B**). An analytical sample was recrystallized from methanol to give yellow leaflets, mp 121-123°; ir (potassium bromide) υ_{max} cm^{-1}: 2900, 2800, 2175 (CN), 1605, 1560, 1520, 1440, 1400, 1360, 1295, 1220, 1190, 1170, 1120, 1090; ^{1}H-nmr (deuteriochloroform) δ: 2.09 (s, 3H, SMe), 2.80 (s, 6H, NMe_2), 2.90 (s, 6H, phenyl-NMe_2), 4.35 (s, 1H, =CH-CN), 5.52 (s, 1H, =CH), 6.67 (d, 2H, 2', 6'-H, J=8.8 Hz), 7.11 (d, 2H, 3', 5'-H, J=9.1 Hz); ms *m/z*: 288 (M^++1, 14), 287 (M^+, 70), 286 (12), 272 (21), 241 (18), 240 (100), 225 (16), 197 (15), 196 (10), 161 (13), 119 (10), 69 (11), 44 (11). *Anal.* Calcd. for $C_{16}H_{21}N_3S$: C, 66.86; H, 7.36; N, 14.62. Found: C, 66.68; H, 7.29; N, 14.56.

5-(4-Dimethylaminophenyl)-3-methylthiopenta-5-pyrrolidino-2,4-dienenitirile (15m). This compound (0.80 g, 2.8 mmoles) was obtained in 51% yield from **3i** (1.43g, 5 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **15a** (**Method B**). An analytical sample was recrystallized from methanol to give yellow leaflets, mp 123-125°; ir (potassium bromide) υ_{max} cm^{-1}: 3090, 2180 (CN), 1610, 1560, 1520, 1480, 1460, 1420, 1380, 1350, 1290, 1200, 1110; ^{1}H-nmr (deuteriochloroform) δ: 1.88 (s, 4, pyrrolidino 3, 4-H), 2.07 (s, 3H, SMe), 3.00 (s, 6H, NMe_2), 3.19 (s, 4H, pyrrolidino 2, 5-H), 4.22 (s, 1H, =CH-CN), 5.59 (s, 1H, =CH), 6.68 (d, 2H, 2', 6'-H, J=8.8 Hz), 7.11 (d, 2H, 3', 5'-H, J=9.1 Hz); ms *m/z*: 314 (M^++1, 10), 313 (M^+, 45), 298 (17), 267 (20), 266 (100), 243 (10), 226 (24), 197 (32), 69 (20), 57 (11), 55 (11), 45 (14), 44 (17), 43 (14). *Anal.* Calcd. for $C_{18}H_{23}N_3S$: C, 68.97; H, 7.40; N, 13.41. Found: C, 69.12; H, 7.25; N, 13.40.

5-(4-Bromophenyl)-3-methylthiopenta-5-pyrrolidino-2,4-dienenitirile (15p). This compound (0.51 g, 1.5 mmoles) was obtained in 29% yield from **3j** (1.61g, 5 mmoles) and 2 ml of pyrrolidine in a manner similar to that described for the preparation of **15a** (**Method B**). An analytical sample was recrystallized from methanol to give yellow leaflets, mp 142-144°; ir (potassium bromide) υ_{max} cm^{-1}: 2960, 2850, 2190 (CN), 1550, 1500, 1420, 1370, 1340, 1280, 1230, 1200, 1180, 1155,

1105, 1065, 1010.; ^{1}H-nmr (deuteriochloroform) δ: 1.89(s, 4H, pyrrolidino 3, 4-H), 2.08 (s, 3H, SMe), 3.14 (s, 4H, pyrrolidino 2, 5-H), 4.30 (s, 1H, =CH-CN), 5.49 (s, 1H, =CH), 7.18 (d, 2H, J=8.5 Hz, 2', 6'-H), 7.50 (d, 2H, 3', 5'-H, J=8.5 Hz); ms *m/z*: 350 (M^++1, 33), 349 (M^+, 9), 348 (34), 333 (16), 304 (18), 303 (98), 302 (20), 301 (100), 269 (11), 263 (17), 261 (20), 222 (26), 154 (10), 153 (40), 149 (11), 140 (10), 71 (12), 70 (38), 58 (17), 57 (11), 55 (16), 47 (10), 45 (10), 44 (63).

Anal. Calcd. for $C_{16}H_{17}N_2SBr$: C, 55.02; H, 4.91; N, 8.02. Found: C, 55.67; H, 5.10; N, 7.69.

X-Ray Experimental Reports of 8a. ***Data Collection.*** A paleyellow prism crystal of $C_{14}H_{12}O_4S$ having approximate dimensions of 0.35 x 0.20 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku with graphite monochromated Mo-Kα radiation. Indexing was performed from 4 stills that were exposed for 15 seconds. The crystal-to-detector distance was 40.70 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions. a =14.137(2)Å, b = 7.0687(7)Å, c = 13.9118(4) Å, V = 1295.4(2) Å^3, β = 111.2830(6)o. For Z = 4 and F.W. = 276.31, the calculated density is 1.42 g/cm3. The systematic absences of: h0l: l ± 2n, 0k0: k ± 2n. uniquely determine the space group to be: P21/c (#14). The data were collected at a temperature of 22 + 1°C to a maximum 2θ value of 55.1°. A total of 464 oscillation images were collected. A sweep of data was done using ω scans from -19.0 to 23.0° in 0.5° step, at χ = 90.0° and ϕ = 0.0°. The exposure rate was 30.0 [sec./°]. The is detector at the zero swing position. A second sweep was performed using ϕ scans from 0.0 to 190.0° in 0.5° step, at ω = 0.0° and χ = 90.0°. The exposure rate was 30.0 [sec./°]. The detector is at the zero swing position. The crystal-to-detector distance was 40.70 mm. Readout was performed in the 0.000 mm pixel mode.

Data Reduction. Of the 11177 reflections that were collected, 2892 were unique (Rint = 0.021); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). Net intensities and sigmas were derived as follows: F2 = [Σ(Pi - mBave)] . Lp-1 where Pi is the value in counts of the ith pixel m is the number of pixels in the integration area B_{ave} is the background average. Lp is the Lorentz and polarization factor. B_{ave} = Σ(Bj)/n where n is the number of pixels in the background area Bj is the value of the jth pixel in counts. σ2(F2hkl) = [(ΣPi) + m((Σ(Bave - Bj)^2)/(n-1))] . Lp . errmul + (erradd . F^2)^2 where erradd = 0.00. errmul = 1.00

The linear absorption coefficient, μ, for Mo-Kα radiation is 2.6 cm^{-1}. was applied which resulted in transmission factors ranging from 0.89 to 1.00. The data were corrected for Lorentz and polarization effects.

X-Ray Experimental Reports of 12l. ***Data Collection.*** A pale greenish yellow crystal of $C_{16}H_{17}N_2O_3$ having approximate dimensions of 0.40 x 0.12 x 0.08 mm was mounted on a glass fiber. All measurements were made on a Rigaku with graphite monochromated Mo-Kα radiation. Indexing was performed from 7 stills that were exposed for 30 seconds. The crystal-to-detector distance was 40.70 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions. a=7.59380(10)Å, b=14.0254(4)Å, c=27.4606(8)Å, V=2924.72(1o)Å[8]. For Z=8 and F.W.=283.33, the calculated density is 1.29g/cm^3. The systematic absences of: h00: h±2n, 0k0:k±2n, 00l:l±2n. uniquely determine the space group to be: $P2_12_12_1$(#19). The data were collected at a temperature of 23±1°C to a maximum 2θ value of 55.0°. A total of 464 oscillation images were collected. A sweep of data was done using ϕ scans from 0.0 to 190.0° in 0.5° step, at ω=0.0° and χ=0.0°. The exposure rate was 50.0[sec./°]. The detector is at the zero swing position. A second sweep was performed using ω scans from-190.0 to 23.0° in 0.5° step, at χ=90.0° and ϕ=0.0°. The exposure rate was 50.0 [sec./°]. The detector is at the zero swing position. The crystal-to-detector distance was 40.70 mm. Readout was performed in the 0.000 mm pixel mode.

Data Reduction. Of the 25309 reflections that were collected, 3775 were unique (Rint=0.050); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). Net intensities and sigmas were derived as follows: m is the number of pixels in the integration area; Bave is the background average; Lp is the Lorentz and polarization factor; B_{ave}= Σ(Bj)/n where n is the number of pixels in the background area. Bj is the value of the jth pixel in counts. $\sigma^2(F^2hkl)$=[(ΣPi + m((ΣB_{ave}-B_j)^2)/(n-1))] · Lp · ermul + (erradd · F^2)^2 where eraadd=0.00, errmul=1.00.

The linear absorption coefficient, μ, for Mo-Kα radiation is 0.9 cm^{-1} was applied which resulted in transmission factors ranging from 0.79 to 1.01. The data were corrected for Lorentz and polarization effects.

X-Ray Experimental Reports of 15b. ***Data Collection.*** A clear prism crystal of $C_{16}H_{18}N_2S$ having approximate dimensions of 0.40 x 0.30 x 0.15 mm was mounted on a glass fiber. All measurements were made on a Rigaku with graphitenmono-chromated Mo-Kα radiation. Indexing was performed from 4531 stills which were exposed for 0 seconds. The crystal-to-detector distance was 40.70 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthhombic cell with dimensions. a=9.6123(13)Å, b=17.055(3)Å, c=9.5000(4)Å, V=1492.6(3) Å^3, β=106.5908(7)°. For Z=4 and F.W.=270.39, the calculated density is 1.20 g/cm^3. The systematic absences of : h00: h±2n, 0k0:k±2n. uniquely determine the space group to be: $P2_1/n$(#14). The data were collected at a temperature of 22±1°C to a maximum 2θ value of 55.0°. A total of 0 oscillation images were collected. The crystal-to-detector distance was 40.70 mm. Redout was performed in the 0.000 mm pixel mode.

Data Reduction. Of the 12846 reflections that were collected, 3353 were unique (Rint=0.030); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). Net intensities and sigmas were derived as follows: F2=[Σ(P_i-mB_{ave})] · Lp^{-1} where P_i is the value in counts of the ith pixel, m is the number of pixels in the intergration area , B_{ave} is the background average, Lp is the Lorentz and polarization factor. B_{ave}=Σ(Bj)/n wehere n is the number of pixels in the background area, B_j is the value of the jth pixel in counts. $\sigma^2(F^2hkl)$=[ΣPi + m((ΣB_{ave}-B_j)^2)/(n-1))] · Lp · ermul + (erradd · F^2)^2 where eraadd=0.00, errmul=1.00.

The linear absorption coefficient, μ, for Mo-Kα radiation is 2.10 cm^{-1}. was applied which resulted in transmission factors ranging from 0.83 to 1.06. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient=181.619995).

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