Anilinopyrylium Salts. Their Synthesis and Conversion to Other Heterocyclic Systems

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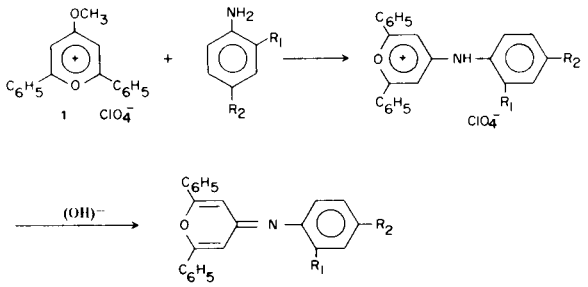
Two methods for the preparation of anilinopyrylium salts are described. The conversion of these salts to pyrans, pyridines, and nitrobenzenes is discussed. Azepines, benzimidazoles, and benxotriazoles are readily obtained from the *o*-aminoanilinopyrylium salts.

In our previous paper we reported the reaction of 4-methoxy-2,6-dimethyl- and 4-methoxy-2,6-diphenylpyrylium perchlorate **1** with secondary amines (1).

The present paper describes the reaction of **1** with aromatic amines. The substituent on the anilino moiety was chosen with the intention of utilizing it as a site for further reaction. Aniline, 4-acetanilide, *o*- and *p*-phenylenediamine, 4-dimethylaminoaniline, and *o*-anisidine react with **1** to give the corresponding pyrylium perchlorates, which, on treatment with bases, give the imino-4*H*-pyrans, as set forth in Scheme I.

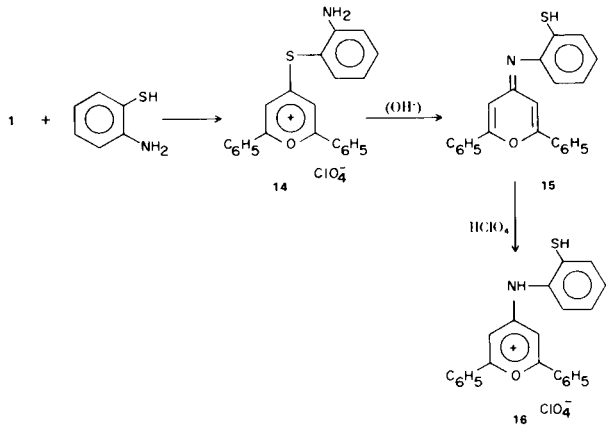
Scheme I



	R_1	R_2	
2	H	H	8
3	H	NHCCH$_3$ (O)	9
4	NH_2	H	10
5	H	NH_2	11
6	H	$N(CH_3)_2$	12
7	OCH_3	H	13

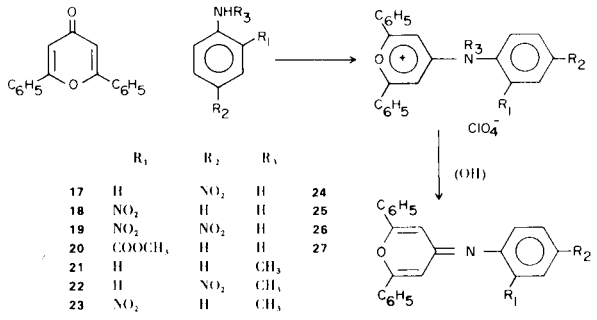
In contrast to the above, *o*-aminobenzenethiol reacts with **1** to give **14**, which, on treatment with potassium hydroxide or dimethylhydrazine, is deprotonated and rearranges to **15**. Protonation of **15** with perchloric acid gives **16**. The presence of a primary amino group in **14** is evidenced by strong absorption in the ir region at 3.1 and 3.2 μ. In **16** the amino absorption disappears and is replaced by a broad absorption centered at 3.5 μ characteristic of thiol absorption. The pyran **15** is thermotropic. Its solution in hot pyridine is deep greenish yellow. On cooling, the solution becomes pale yellow.

Scheme II



Anilines which contain an electron-withdrawing group in the *ortho* or *para* position do not react with **1** but do react with 2,6-diphenyl-4-pyrone in the presence of phosphoryl chloride to give anilinopyrylium salts. Typical amines that behave in this manner are *o*- and *p*-nitro-

Scheme III



	R_1	R_2	R_3	
17	H	NO_2	H	24
18	NO_2	H	H	25
19	NO_2	NO_2	H	26
20	$COOCH_3$	H	H	27
21	H	H	CH_3	
22	H	NO_2	CH_3	
23	NO_2	H	CH_3	

anilines, 2,4-dintroaniline, methyl anthranilate, *N*-methylaniline, and *N*-methyl *o*- and *p*-nitroanilines. Scheme III shows a tabulation of the perchlorate salts and their corresponding imino-4*H*-pyrans, which are obtained by treating the pyridine solution of the salts with methanolic potassium hydroxide. The salts can be crystallized from pyridine-methanol without change.

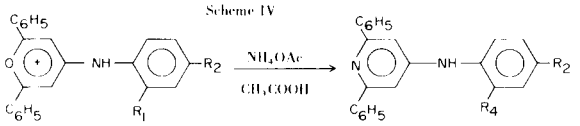
With perchloric acid in acetic acid the iminopyrans regenerate the pyrylium salts from which they were obtained. No rearrangement occurs. The perchlorate salt **22** was also prepared from **24** and methyl fluorosulfonate in chloroform.

Representative pyrylium salts chosen from Schemes I, II, and III were treated with ammonium acetate in acetic acid with the following results:

Compounds **7** and **16** required at least 24 hours for conversion to the pyridine derivative **29** and the acetylated pyridine **30**, respectively. No replacement of the hetero oxygen by nitrogen occurred. Compounds **28** and **29** were obtained as the pyridinium salts from the reaction mixture and required the use of methanolic potassium hydroxide to liberate the free base. The salt **5** undergoes acetylation to give **3**. The formation of **31**, **32**, and **33** occurred within 2 hours and these products separated as the free base.

The salt **2** could only be converted to the pyridine **28** by reaction with ammonia in pyridine at 150° for 6 hours. It separates as the perchlorate salt. It is, however, contaminated with about 5% of 4-amino-2,6-diphenlypyridine, as shown by mass spectral analysis. The free base **28** was obtained from the perchlorate salt with potassium hydroxide.

Scheme IV

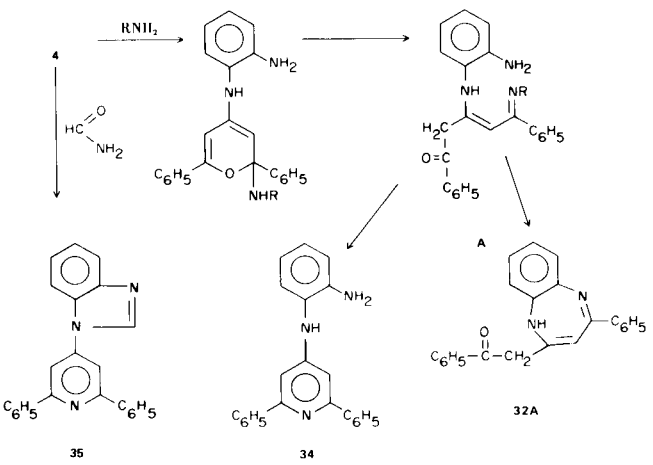


	R_1	R_2	
2	H	H	28
7	OCH_3	H	29
5	See text		3
16	$\overset{O}{\overset{\|}{S}}CH_3$	H	30
18	NO_2	H	31
19	NO_2	NO_2	32
17 (or 24)	H	NO_2	33

The *o*-aminoanilinopyrylium salt **4** remains unchanged after 24 hour's reflux in an acetic acid solution of ammonium acetate. With ammonia in pyridine we usually obtained the azepine **32A**, but once obtained the pyridine derivative **34**. With dimethylhydrazine **32A** is invariably formed in better than 90% yield. The structure of **32A** was determined by means of mass spectral and nmr analysis, the details of which are described in the experimental section and support the assigned structure.

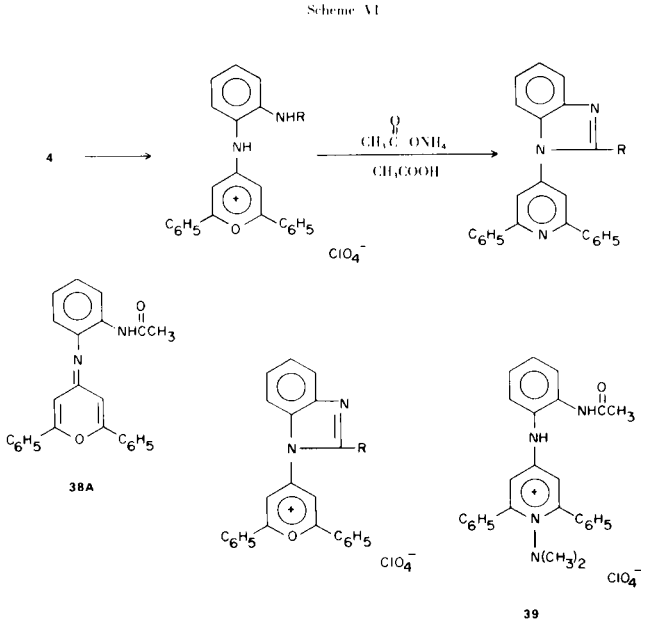
We believe that the initial reaction is the addition of the amine to the pyrylium salt followed by ring opening to give the intermediate A, which subsequently undergoes ring closure to give either the azepine **32A** or the pyridine derivative **34**. With dimethylhydrazine, ring closure to **34** is sterically hindered so that **32A** is formed exclusively.

Scheme V



With formamide the hetero oxygen of **4** is replaced by a nitrogen atom but the amino group also reacts with the formamide, resulting in the formation of the benzimidazole **35** (see Scheme V). The latter compound also may be obtained by the formylation of **4** to give **36** which, on treatment with ammonium acetate in acetic acid, gives **35**. The acetyl derivative **37** and its corresponding pyridine derivative **38** were prepared in an analogous manner. We were unable to effect ring closure of **36** or **37** to a benzimidazole with acetic anhydride or phosphoryl chloride.

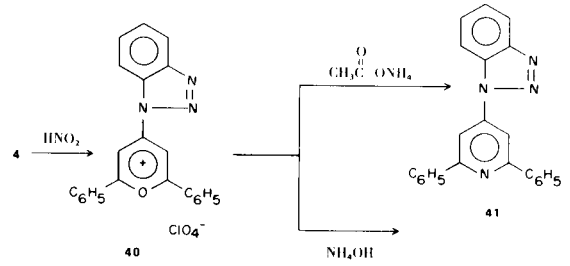
Scheme VI



With ammonia in pyridine, **37** gave the pyran **38A**, which was also obtained by the acetylation of **10**. With dimethylhydrazine **37** gave the pyridinium salt **39**.

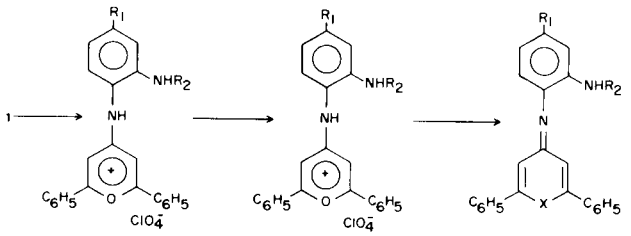
Because we could not obtain 4-(benzimidazol-1-yl)-2,6-diphenylpyrylium perchlorate from **36** and because this type of compound was required for another problem, we prepared an analogous compound by treating **4** with nitrous acid and obtained **40**. The pyridine **41** is readily obtained from **40** with ammonium acetate in acetic acid. With ammonia in pyridine a product B of mass 569 is obtained, the structure of which has not been established.

Scheme VII



With the intention of extending the scope of these reactions, 4-chloro- and 4-nitro-*o*-phenylenediamine were allowed to react with **1** to give **42** and **43**, respectively. Formylation and acetylation yielded **44** and **45**, which, on treatment with base, gave the aminopyrans **46** and **47**. Treatment of **45** with ammonia in pyridine give **48**.

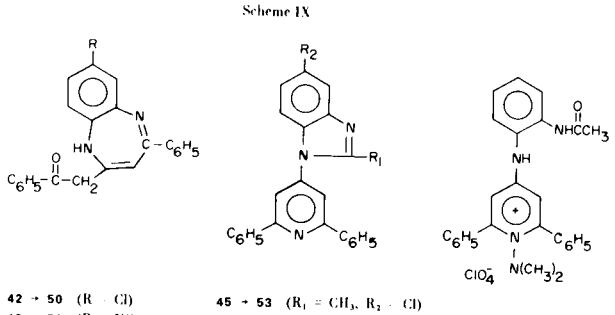
Scheme VIII



42 (R_1 = Cl, R_2 = H)
43 (R_1 = NO_2, R_2 = H)
44 (R_1 = Cl, R_2 = CHO)
45 (R_1 = Cl, R_2 = CH_3CO)

46 (X = O, R_1 = Cl, R_2 = CHO)
47 (X = O, R_1 = Cl, R_2 = CH_3CO)
48 (X = NH, R_1 = Cl, R_2 = CH_3CO)
49 (R_1 = NO_2, R_2 = CHO)

Scheme IX



42 → **50** (R = Cl)
43 → **51** (R = NO_2)

45 → **53** (R_1 = CH_3, R_2 = Cl)
49 → **54** (R_1 = H, R_2 = NO_2)

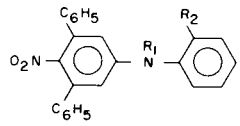
52

The pyrylium salts **42** and **43** react with dimethylhydrazine to give the azepines **50** and **51**, respectively, whereas the acetyl derivative **37** with the same reagent gives the pyridine salt **52**. The pyrylium salts **45** and **49** react with ammonium acetate in acetic acid to give the benzimidazole derivatives **53** and **54**, respectively.

Attempts to form analogs of **40** by diazotization of **42** and **43** in methanol resulted in the replacement of the anilino moiety with a methoxy group. The resultant product is 4-methoxy-2,6-diphenylpyrylium perchlorate **1**.

Nitromethane reacts readily with **7** and **21** to give the substituted nitrobenzenes **55** and **56**, respectively, a reaction typical of pyrylium salts.

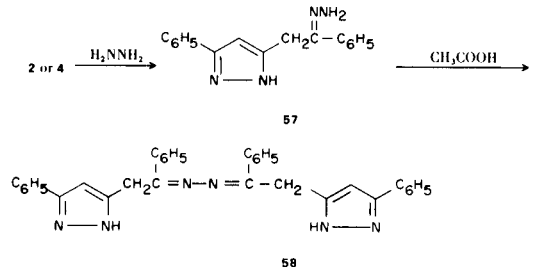
Scheme X



7 + CH_3NO_2 → **55** (R_1 = H, R_2 = OCH_3)
21 + CH_3NO_2 → **56** (R_1 = CH_3, R_2 = H)

The reaction of **2** and **4** with hydrazine gives the pyrazole **57**, which has been prepared previously (1). Crystallization of **57** from acetic acid gives the azine **58**. The pyrazole **57** has also been obtained by the action of hydrazine on 4-dicyanomethylene-2,6-diphenyl-4*H*-pyran, 4-piperidyl-2,6-diphenylpyrylium perchlorate, 2,6-diphenylpyrone, 4-methoxy-2,6-diphenylpyrylium perchlorate and 1,5-diphenyl-1,3,5-pentanetrione.

Scheme XI

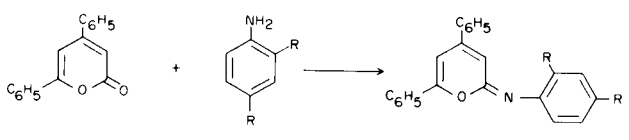


57

58

4,6-Diphenyl-2-pyrone reacts with aniline and 2,4-dinitroaniline in the presence of phosphoryl chloride in the same manner as the 4-pyrones to give the iminopyrans **59** and **60**.

Scheme XII



59 R = H
60 R = NO_2

TABLE I

Physical Data

	Empirical Formula	Calcd. C	H	N	Cl	Found C	H	N	Cl	M. P. Solvent of Recrystn.	Method of Prepn.	Yield, %
1	Ref. 1											
2	$C_{23}H_{18}ClNO_5$	65.2	4.3	3.3	8.3	65.0	4.4	3.3	8.3	140 (e)	A	90
3	$C_{25}H_{21}ClN_2O_6$	62.5	4.4	5.9	7.3	62.3	4.4	6.0	7.5	150 (c)	A (1); D	86
4	$C_{23}H_{19}ClN_2O_5$	63.0	4.3	6.4	8.0	63.2	4.4	6.5	8.4	240 (e)	A	98
5	$C_{23}H_{19}ClN_2O_5$	63.0	4.3	6.4	8.0	62.8	4.7	6.1	8.2	278 (j)	A	97
6	$C_{25}H_{23}ClN_2O_5$	64.5	5.0	6.0	7.5	64.2	4.7	5.8	7.2	230 (c)	A	85
7	$C_{24}H_{20}ClNO_6$	63.6	4.4	3.1	7.7	63.3	4.5	3.3	7.5	243 (c)	A	77
8	$C_{23}H_{17}NO$	85.2	5.3	4.3		85.2	5.4	4.5		137 (b)	C (4)	87
9	$C_{25}H_{20}N_2O_2$	79.0	5.3	7.4		78.6	5.1	7.7		218 (b)	C	68
10	$C_{23}H_{18}N_2O$	81.7	5.3	8.3		81.3	5.3	8.3		165 (a + b)	C (2)	81
11	$C_{23}H_{18}N_2O$	81.7	5.3	8.3		81.7	5.7	8.2		218 (a + b)	C	63
12	$C_{25}H_{22}N_2O$	82.0	6.0	7.7		81.7	5.7	8.2		115 (a + b)	C	68
13	$C_{24}H_{19}NO_2$	81.7	5.4	4.0		81.9	5.7	3.6		120 (f)	C	71
14	$C_{23}H_{18}ClNO_5S$	60.7	4.0	3.1	7.7	60.5	4.1	2.8	7.4	195 (c)	A	86
15	$C_{23}H_{17}NOS$	77.7	4.8	3.9		77.8	4.8	3.8		170 (a +b)	C (4)	93
16	$C_{23}H_{18}ClNO_5S$	60.7	4.0	3.1	7.7	60.4	3.8	3.0	7.8	210 (k)	-- (5)	76
17	$C_{23}H_{17}ClN_2O_7$	59.0	3.6	6.0	7.5	59.0	3.8	6.2	7.5	322 (e)	B	91
18	$C_{23}H_{17}ClN_2O_7$	59.0	3.6	6.0	7.5	58.7	4.0	6.3	7.8	242 (d)	B (4)	89
19	$C_{23}H_{16}ClN_3O_9$	53.7	2.9	8.2		54.1	3.2	8.0		314 (d)	B	67
20	$C_{25}H_{20}ClNO_7$	62.3	3.8	2.9	7.3	62.0	4.3	3.0	7.4	165 (c)	B	56
21	$C_{24}H_{20}ClNO_5$	65.8	4.6	3.2	8.0	65.4	4.4	3.4	8.0	210 (a + b)	B (3)	88
22	$C_{24}H_{19}ClN_2O_7$	59.7	4.0	5.8		59.4	4.0	5.9		291 (c)	B	83
23	$C_{24}H_{19}ClN_2O_7$	59.7	4.0	5.8	7.3	59.9	4.2	6.0	7.2	300 (d)	B	67
24	$C_{23}H_{16}N_2O_3$	75.1	4.4	7.6		75.5	4.5	7.6		182 (a + b)	C	77
25	$C_{23}H_{16}N_2O_3$	75.1	4.4	7.6		75.4	4.4	7.6		155 (c)	C (4)	86
26	$C_{23}H_{15}N_3O_5$	66.8	3.6	10.0		67.2	3.7	10.0		210 (e)	C	91
27	$C_{25}H_{19}NO_3$	78.7	5.0	3.7		78.5	5.1	3.6		150 (f)	C	76
28	$C_{23}H_{18}N_2$	85.6	5.6	8.7		85.4	5.4	8.5		140 (b +g)	- (5)	52
29	$C_{24}H_{20}N_2O$	81.7	5.7	8.0		81.6	5.8	8.0		109 (f)	C	47
30	$C_{25}H_{20}N_2OS$	75.6	5.0	S = 8.1		75.4	4.9	S = 7.9		195 (h)	D	54
31	$C_{23}H_{17}N_3O_2$	75.0	4.6	11.4		74.6	5.0	11.5		145 (i)	D	42
32	$C_{23}H_{17}N_3O_2$	75.0	4.6	11.4		74.8	4.7	11.8		110 (h + f)	D	67
32A	$C_{23}H_{18}N_2O$	81.7	5.3	8.3		81.6	5.5	8.6		185 (h)	E	88
33	$C_{23}H_{16}N_4O_4$	67.0	3.9	13.6		67.0	4.0	14.0		227 (d)	D	92
34	$C_{23}H_{19}N_3$	81.9	5.6	12.4		81.5	5.9	12.3		158 (e)	– (5)	83
35	$C_{24}H_{17}N_3$	83.0	4.9	12.0		82.8	5.0	12.0		188 (e)	D	64
36	$C_{24}H_{19}ClN_2O_6$	61.8	4.1	6.0		61.9	4.2	6.0		278 (d)	F	81
37	$C_{25}H_{21}ClN_2O_6$	62.5	4.3	5.8	7.4	62.7	4.3	5.8		244 (d)	F	83
38	$C_{25}H_{19}N_3$	83.2	5.3			83.0	5.6			195 (b)	D	78
38A	$C_{25}H_{20}N_2O_2$	78.9	5.2	7.4		79.0	5.1	7.5		206 (e)	C	69
39	$C_{27}H_{27}ClN_4O_5$	62.2	5.2	10.8		62.0	5.3	10.9		260 (b)	-- (5)	74
40	$C_{23}H_{16}ClN_3O_5$	61.2	4.0	9.3		61.1	4.0	9.3		220 (d)	– (5)	88
41	$C_{23}H_{16}N_4$	79.3	4.6	16.1		79.5	5.0	16.3		140 (i)	D	68
42	$C_{23}H_{18}Cl_2N_2O_5$	58.6	3.8	5.9	14.8	58.5	3.9	6.0	14.6	234 (e)	A	82
43	$C_{23}H_{18}ClN_3O_7$	57.3	3.7	8.7		57.4	4.0	8.6		235 (j + g)	A	81
44	$C_{24}H_{18}Cl_2N_2O_6$	57.4	3.6	5.6		57.7	4.0	5.4		260 (a + b)	F	86
45	$C_{25}H_{20}Cl_2N_2O_6$	58.2	3.9	5.5		58.2	3.8	5.4		300 (c)	F	88
46	$C_{24}H_{17}ClN_2O_2$	72.1	4.2	7.0		71.8	4.5	7.2		230 (e)	C	74
47	$C_{25}H_{19}ClN_2O_2$	72.4	4.5	6.7		72.3	4.5	7.0		210 (c)	C	84
48	$C_{25}H_{20}ClN_3O$	72.6	4.8	10.1		72.9	5.2	10.2		208 (e)	D	70
49	$C_{24}H_{18}ClN_3O_8$	56.4	3.5	8.2		56.3	3.5	8.2		250 (c)	F	88
50	$C_{23}H_{17}ClN_2O$	74.5	4.3	9.6		74.3	4.5	9.7		193 (h)	E	91

TABLE I (continued)

Physical Data

	Empirical Formula	Calcd. C	H	N	Cl	Found C	H	N	Cl	M. P. Solvent of Recrystn.	Method of Prepn.	Yield, %
51	$C_{23}H_{17}N_3O_3$	72.1	4.5	10.9		71.6	4.6	10.9		230 (a + b)	E	84
52	$C_{27}H_{27}ClN_4O_5$	62.2	5.3	10.8		62.0	5.3	10.9		260 (b)	(5)	77
53	$C_{25}H_{18}ClN_3$	76.0	4.5	10.5		76.0	4.8	10.5		228 (e)	D	68
54	$C_{25}H_{16}N_4O_2$	73.4	4.1	14.3		73.3	4.0	14.2		211 (e)	D	89
55	$C_{25}H_{20}N_2O_3$	75.8	5.0	7.1		76.2	5.2	7.3		170 (b)	(5)	66
56	$C_{25}H_{20}N_2O_2$	79.2	5.3	7.4		79.0	5.5	7.5		154 (b)	(5)	62
57	$C_{17}H_{16}N_4$	73.9	5.8	20.3		73.6	6.1	20.2		176	(5)	68
58	$C_{34}H_{28}N_6$	78.5	5.4	16.0		78.3	5.7	15.8		234 (k)	(5)	84
59	$C_{23}H_{17}NO$	85.5	5.3	4.3		85.4	5.5	4.0		140 (a + b)	B	
60	$C_{23}H_{15}N_3O_5$	53.7	2.9	8.2		53.6	3.0	8.1		200 (a + b)	B	

(1) Also made by reaction of **5** with ammonium acetate in acetic acid in 68% yield. (2) With perchloric acid in acetic acid **10** gives a bisperchlorate, m.p. 290°, which regenerated 4 on crystallization from pyridine methanol. (3) Also obtained by methylation of 24 with methyl fluorosulfonate. (4) The electronic spectra for the compounds were determined in acetonitrile (λ max $\epsilon \times 10^{-3}$); **8** 262 (17.5), 328 (22.5); **25** 238 (38.0), 266 (43.0), ~360 (13.7); **18** 262 (18.0), 332 (20.0); **15** 244 (21.0), 272 (22.0), 370 (6.7). (5) See Expermental. (a) Pyridine; (b) methanol; (c) acetonitrile; (d) formic acid; (e) nitromethane; (f) ligroin; (g) water; (h) toluene; (i) butanol; (j) dimethylformamide; (k) acetic acid.

EXPERIMENTAL

The following general procedures are illustrated by an example. Analogous compounds were prepared in a similar manner and are so indicated in Table I by the appropriate letter. Where no letter occurs in the preparation column of Table I, a procedure is given in the Experimental section. The analytical results, melting points, yields, and solvents of crystallization are collected in Table I.

Procedure A. 4-Anilino-2,6-diphenylpyrylium Perchlorate (**2**).

A solution of 34.6 g. (0.1 mole) of 4-methoxy-2,6-diphenylpyrylium perchlorate (**1**) and 10 ml. (0.11 mole) of aniline in 200 ml. of acetonitrile was heated under reflux for 24 hours, then cooled to 10-15°. The solid was collected giving 38 g. (90%) of **2**. The crude product is sufficiently pure for most subsequent reactions.

Procedure B. 4-(4-Nitroanilino)-2,6-diphenylpyrylium Perchlorate (**17**).

A mixture of 2.5 g. (0.01 mole) of 2,6-diphenyl-4-pyrone and 1.5 g. (0.01 mole) of *p*-nitroaniline in 6 ml. of phosphoryl chloride was heated to 90-95° for 2 hours. The reaction mixture was poured into 50 ml. of methanol and 2 ml. of 70% perchloric acid was added. The yellow product was collected and washed with methanol.

Procedure C. 4-Phenylimino-2,6-diphenyl-4*H*-pyran (**8**).

A solution of 4.3 g. (0.01 mole) of **2** in 25 ml. of pyridine was treated with 15 ml. of a saturated solution of potassium hydroxide in methanol and heated under reflux for 5 minutes. An additional 40 ml. of methanol was added. After cooling, the solid was collected.

Procedure D. 4-(2-Nitroanilino)-2,6-diphenylpyridine (**32**).

A mixture of 2.34 g. (0.005 mole) of **18** and 5 ml. of ammonium acetate in 15 ml. of acetic acid was heated under reflux for 2 hours. Water was added to the reaction mixture and the precipitate was collected.

4-(4-Acetamidoanilino)-2,6-diphenylpyrylium Perchlorate (**3**).

Under the same conditions as above, **5** gave **3**.

1-(2,6-Diphenyl-4-pyridyl)benzimidazole (**35**).

This material was prepared from **36** using Procedure D. It is also obtained by refluxing **4** in formamide for 1 hour.

Procedure E. 2-Phenacyl-4-phenyl-1*H*-1,5-diazepine (**32A**).

A solution of 2.14 g. (0.005 mole) of **4** in 10 ml. of acetonitrile containing 2 ml. of dimethylhydrazine was heated at reflux for 1 hour. The product that separated from the hot solution was collected and crystallized from toluene to give 1.47 g. (88%) of **32A**. The nmr spectrum in deuteriochloroform shows the two methylene protons at 190 cps and the vinyl proton at 335 cps. The mass spectrum shows 338 (100%) [M], 337 (38) [M-1], 233 (47) [M-C_6H_5CO], 194 (23) [233-CO], 105 (36) C_6H_5CO.

Procedure F. 4-(2-Acetamidoanilino)-2,6-diphenylpyrylium Perchlorate (**37**).

A mixture of 10 g. of **4** in 35 ml. of acetic anhydride was heated on the steam bath for 2 hours. After cooling, the product was collected to give 10.5 g. (96%), m.p. 240° from nitromethane.

4-(2-Formylaminoanilino)-2,6-diphenylpyrylium Perchlorate (**36**) was prepared in a similar manner. Formic acid was used instead of acetic anhydride.

4-(2-Aminoanilino)-2,6-diphenylpyridine (**34**).

A solution of 2.2 g. (0.005 mole) of **4** in 10 ml. of pyridine containing 5 ml. of 28% ammonium hydroxide was refluxed for 24 hours and 20 ml. of methanol was added. On cooling, 1.4 g. (83%) of **34** separated, m.p. 158°.

4-(Benzotriazol-1-yl)-2,6-diphenylpyrylium Perchlorate (**40**).

A solution of 4.4 g. (0.01 mole) of **4** in 120 ml. of methanol and 15 ml. of hydrochloric acid was cooled to 15° and 3.0 g. of sodium nitrite in 15 ml. of water was slowly added with stirring. The product, which precipitated immediately, was collected and crystallized from formic acid.

4-(4-Nitro-*N*-methylanilino)-2,6-diphenylpyrylium Perchlorate (**22**).

Compound **24**, 1 g. in 30 ml. of chloroform and 2 ml. of methyl fluorosulfonate, was heated to reflux for 10 minutes. After 24 hours, the white crystals were filtered off, dissolved in formic acid, and 1 ml. of 70% perchloric acid was added. The product, 0.8 g., m.p. 275-278°, was collected.

4-Anilino-2,6-diphenylpyridine (**28**).

A solution of 5.0 g. of **2** in 250 ml. of pyridine and 20 ml. of 28% ammonium hydroxide was heated to 150° under pressure in a bomb for 6 hours. The solvent was evaporated and the residual viscous oil was triturated with acetic acid. The bisperchlorate was collected and crystallized from acetonitrile. Yield 3.2 g., m.p. 210°.

Anal. Calcd. for $C_{23}H_{18}N_2 \cdot HClO_4$: C, 65.6; H, 4.3; N, 6.7. Found: C, 65.6; H, 4.9; N, 6.8.

A solution of 1 g. of bisperchlorate in 12 ml. of pyridine and 5 ml. of methanolic potassium hydroxide gave 0.4 g. of **28**. Mass spectral peaks 322 (63%) [m] 321 (59%), 246 (12%).

4-(2-Mercaptoanilino)-2,6-diphenylpyrylium Perchlorate (**16**).

A solution of 2 g. of **15** in 10 ml. of hot acetic acid was treated with 4 ml. of 70% perchloric acid. After cooling, the product was collected and crystallized from acetic acid. Yield 1.3 g., m.p. 210°.

N-(2-Nitro-*m*-terphenyl-5-yl)-*o*-anisidine (**55**).

A solution of 2.3 g. (0.005 mole) of **7** in 15 ml. of nitromethane and 5 ml. of diisopropylethylamine was refluxed for 2 hours and evaporated to dryness. Crystallization from ethanol gave **55**.

N-(2-Nitro-*m*-terphenyl-5-yl)-*N*-methylaniline (**56**) was prepared from **21** and nitromethane as above.

3-Phenylpyrazolyl-5-methylphenyl Ketone (**57**).

A mixture of 1.0 g. of **3** (or **4**) and 3.0 ml. of 64% hydrazine in 10 ml. of alcohol was heated under reflux for 15 minutes. On cooling, 0.3 g. of **57** separated. The ir spectrum of **57** is identical with that of an authentic sample (1).

α-(3-Phenyl-5-pyrazolylmethyl)benzylideneazine (**58**).

A mixture of 2.0 g. of 1,5-diphenyl-1,3,5-pentanetrione and 5 ml. of 64% hydrazine in 10 ml. of alcohol was heated for 2 hours on a steam bath. Water was added to the reaction mixture and the precipitate was collected and crystallized from acetic acid to give 1.1 g. of **58**, m.p. 234°. This same product is obtained by crystallizing **57** from acetic acid. The principal fragments obtained in the mass spectrometer, 520 (48%) [M^+] 400 (6.3) 378 (100), are consistent with the ketal structure.

4-(2-Acetamidoanilino)-2,6-diphenyl-4-dimethylaminopyridinium Perchlorate (**39**).

A mixture of 4.0 g. of **37** in 50 ml. of acetonitrile and 12 ml. of dimethylhydrazine was heated under reflux for 2 hours, after which 50 ml. of water was added. On cooling, the precipitate was collected and crystallized from alcohol.

REFERENCES

(1) J. A. Van Allan, G. A. Reynolds, and C. C. Petropoulos, *J. Heterocyclic Chem.*, **9**, 783 (1972).