Pyranylidene Iminium Salts. I. Iminium Salts Derived from Alkyl-Substituted Pyrylium Salts and Their Hydrolysis Products

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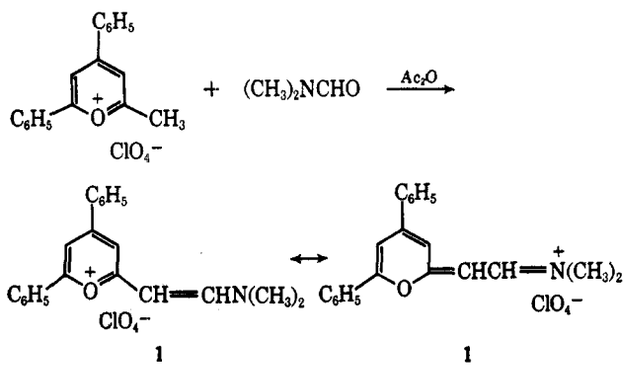
Pyrylium salts containing an active methyl group give monoiminium salts with N,N-dimethylformamide in acetic anhydride and bisiminium salts with the Vilsmeier complex. Methylene pyrylium salts yield monoiminium salts with the Vilsmeier complex. Monoiminium salts are obtained from alkylpyrylium salts and either N,N-dimethylthioacetamide in acetic anhydride or N,N-dialkylamides in the presence of phosphorus oxychloride. Vinylogs of certain of the monoiminium salts are obtained from alkylpyrylium compounds and diethylaminoacrolein in acetic anhydride. The iminium salts are hydrolyzed to give, in most cases, aldehydes and ketones. The hydrolysis products obtained from the iminium salt derived from 2-methyl-4,6-diphenylpyrylium perchlorate are 2-formylmethylidene-4,6-diphenyl-2H-pyran, 4-dimethylamino-2-phenylbenzophenone, and 4-methoxy-2-phenylbenzophenone.

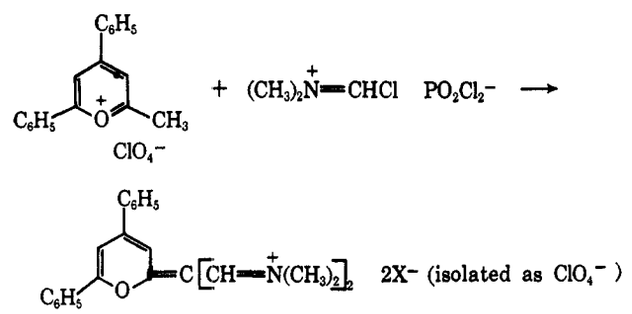
As suggested by the results of earlier work with *p*-dimethylaminobenzaldehyde,[1] it was not surprising to learn than N,N-dimethylformamide reacted with 2-methyl-4,6-diphenylpyrylium perchlorate in acetic anhydride to yield the expected 2-N,N-dimethylaminovinyl derivative **1**.[2] The generality of the reaction with



1 **1**

N,N-dimethylformamide was demonstrated by the formation of the related compounds **2–7** (see Table I). Attempts to extend the reaction through the use of N,N-dimethylacetamide under the same conditions were unsuccessful.[3] However, N,N-dimethylthioacetamide furnished the desired iminium derivatives readily, as shown by the synthesis of **9–12** (Table I). Vinylogs related to **1** were prepared either through the use of dialkylaminoacrolein or its closely related methoxyiminium derivative[4] (see **13–18** in Table I).

Under Vilsmeier–Haack conditions, 2 mol of N,N-dimethylformamide–phosphorous oxychloride complex reacted with 1 mol of the methyl pyrylium salts to give bisiminium salts (**19–23**, Table I) as illustrated below for **19**. Similar behavior has been observed in other instances.[5] Other N,N-disubstituted amides and phosphorous oxychloride led to monoiminium salts (see **9–12** and **24–29**, Table I). We feel that the course of bisiminium salt formation is accounted for by Scheme I. The facts that methylpyrylium salts gave bisiminium salts and that monoiminium salts gave bisiminium salts with the Vilsmeier reagent suggested that this reagent reacts more readily with monoiminium salts than with methylpyrylium salts. Ethylpyrylium salts reacted with the Vilsmeier reagent to form monoiminium salts, and isopropylpyryliam salts failed to react. The formation of monoiminium salts by the reaction of the phosphorous oxychloride complex of other N,N-disubstituted amides with methylpyrylium salts may be the result of steric effects.



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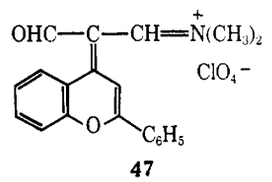
Iminium salts are usually readily hydrolyzed to aldehydes, and the Vilsmeier–Haack procedure often yields an aldehyde owing to hydrolysis of the intermediate iminium salt during the work-up. The iminium salts described in this paper are quite stable, but they are hydrolyzed by strong bases. In most cases, hydrolysis of various iminium salts gave the expected aldehydes or ketones, and the hydrolysis products, **30–46**, are recorded in Table II.

The bisiminium salt **20** was hydrolyzed by methanolic potassium hydroxide to give the bisaldehyde **44**. Hydrolysis of **21** by the same procedure gave the monoaldehyde **47**. A possible explanation for the failure of



47

21 to yield a bisaldehyde on hydrolysis is that **47** is stabilized by resonance to such an extent that the imino bond is no longer reactive. When **20** was heated with

(1) R. Wizinger and K. Wagner, *Helv. Chim. Acta*, **34**, 2290 (1951).

(2) We will use the iminium structures for the compounds described in this paper.

(3) Only 4-methylflavylium perchlorate gave a product with dimethylacetamide in acetic anhydride, and the product was shown to be the pyrylium cyanine dye 4-[3-(4H-flaven-4-ylidene)-2-methyl-1-propenyl]-flavylium perchlorate rather than an iminium salt.

(4) H. Brodereck, F. Effenberger, and G. Simchen, *Chem. Ber.*, **96**, 1350 (1963).

(5) Z. Arnold, *Coll. Czech. Chem. Comm.*, **28**, 863 (1963); H. V. Hansen, J. A. Caputo, and R. I. Meltzer, *J. Org. Chem.*, **31**, 3845 (1966).

TABLE I
METHODS OF PREPARATION AND PHYSICAL PROPERTIES OF IMINIUM SALTS

Compd number	Structure[a]	Method of preparation	Yield, %	Empirical formula	Anal. Calcd, % C	Anal. Calcd, % H	Anal. Found, % N or Cl	Solvent of recrystallization	Mp, °C	Absorption spectra in acetonitrile, λ,mμ (ε × 10⁻³)
1	A-1	A	38	$C_{21}H_{20}ClNO_5$	62.8	5.0	3.5	alcohol	243–244	239 (17.6) 476 (21.2)
					62.9	5.3	3.4			316 (40.7)
2	A-2	A and C	73; 67	$C_{22}H_{22}ClNO_5$	63.5	5.3	3.4	acetonitrile	261–262	241 (15.2) ~366 (9.9)
					63.2	5.2	3.1			313 (21.8) 380 (16.2)
										356(9.6)
3	C-1	A	91	$C_{24}H_{24}ClNO_5$	65.2	5.5	(Cl) 8.0	acetic	275	238 (16.6) 353 (9.5)
					65.5	5.7	(Cl) 8.3	anhydride		305 (30.0) 493 (18.5)
4	B-1	A	90	$C_{21}H_{20}ClNO_5$	62.8	5.0	3.5	acetonitrile	261–262	226 (15.7) 422 (41.5)
					63.0	5.1	3.7			~252 (12.7) 443 (39.8)
										~264 (12.3) 544 (13.9)
										336 (17.1)
5	D-1	A	76	$C_{19}H_{18}ClNO_5$	60.7	4.8	(Cl) 9.5	formic and	240–241	241 (19.3) 428 (39.5)
					60.5	5.0	(Cl) 9.8	acetic acid		268 (8.3) 450 (31.3)
										320 (14.2)
6	D-2	A	42	$C_{19}H_{18}ClNO_4S$	58.2	4.6	(S) 8.2	acetonitrile	186–187	244 (23.0) 326 (13.2)
					58.5	4.7	(S) 8.2			264 (16.2) 464 (35.8)
										284 (8.3)
7	E-1	A and C	82; 70	$C_{20}H_{20}ClNO_5$	61.6	5.2	(Cl) 9.1	acetonitrile	279–280	217 (42.2) 350 (7.2)
					61.3	4.9	(Cl) 8.9			254 (23.2) 368 (6.7)
										288 (14.7) 462 (27.0)
										327 (11.1) 468 (28.1)
										518 (14.7)
8[b]	A-3	A	42	$C_{22}H_{20}ClNO_5$	61.5	4.7	3.3	acetonitrile	240–241	255 (25.6) ~310 (12.0)
					61.7	4.7	3.1			280 (23.2)
9	A-4	B and D	39; 54	$C_{23}H_{22}ClNO_5$	63.5	5.3	3.4	acetonitrile	242–244	237 (15.3) 466 (20.3)
					63.5	5.1	3.2			310 (32.3) 484 (19.6)
10	B-2	B and D	43; 60	$C_{23}H_{22}ClNO_5$	63.5	5.3	(Cl) 8.5	acetonitrile	302–303	247 (13.2) 328 (10.7)
					63.7	5.0	(Cl) 8.3			273 (10.2) 420 (24.0)
11	C-2	B	46	$C_{25}H_{26}ClNO_5$	65.8	5.7	3.1	acetic	212–213	239 (16.2) 374 (5.9)
					65.8	5.6	2.9	anhydride		278 (18.0) 465 (9.0)
										360 (6.3)
12	D-3	B and D	90; 81	$C_{20}H_{20}ClNO_5$	61.6	5.2	3.6	acetonitrile	195–196	237 (19.2) 310 (13.8)
					61.4	5.4	3.3			274 (6.2) 522 (27.1)
13	A-5	E	52	$C_{25}H_{26}ClNO_5$	65.8	5.8	3.1	acetonitrile	201–202	263 (18.2) ~397 (15.2)
		F	78		66.0	5.9	3.0			~300 (14.4) 558 (36.1)
										325 (26.8) 595 (35.4)
14	B-3	E	96	$C_{25}H_{26}ClNO_5$	65.8	5.8	3.1	acetonitrile	210–211	234 (14.7) 340 (14.9)
					66.1	5.6	2.9			248 (14.2) 516 (76.3)
										274 (5.1) 549 (72.5)
										285 (4.9)
15	B-4	E	88	$C_{25}H_{26}ClNO_4S$	63.6	5.6	3.0	ethyl alcohol	185–186	243 (20.0) 339 (10.4)
					63.6	5.4	2.8			286 (6.5) 540 (67.0)
										302 (6.2) 576 (54.6)
16	C-3	E	66	$C_{29}H_{30}ClNO_5$	67.7	6.3	2.8	ethyl alcohol	240–241	262 (14.4) 424 (15.9)
		F	89		67.9	6.0	2.7			326 (24.9) 570 (34.8)
										~340 (20.1) 605 (26.1)
										408 (12.2) ~652 (18.9)
17	D-4	E	72	$C_{23}H_{22}Cl_2NO_5$	59.5	5.0	(Cl) 15.3	acetonitrile	250–251	248 (21.6) 513 (50.5)
					59.7	5.2	(Cl) 14.9			320 (17.5) ~543 (33.2)
										~333 (14.4) 715 (2.1)
18	F-1	E	81	$C_{27}H_{26}ClNO_5$	67.6	5.5	(Cl) 7.4	acetonitrile	207–207.5	244 (32.8) 367 (13.0)
					67.9	5.7	(Cl) 7.4			268 (23.6) 518 (50.5)
										301 (7.7)
19	A-6	C	83	$C_{24}H_{26}Cl_2N_2O_9$	51.7	4.7	(Cl) 12.7	acetonitrile	240–241	244 (13.5) 343 (31.4)
					51.5	5.0	(Cl) 12.9			315 (32.4) 472 (24.0)
20	B-5	C	94	$C_{24}H_{26}Cl_2N_2O_9$	51.7	4.7	(Cl) 12.7	formic acid +	265–266	268 (13.9)
					51.4	5.0	(Cl) 12.7	acetic acid		355 (25.9)
										430 (46.0)
21	D-5	C	73	$C_{22}H_{24}Cl_2N_2O_9$	49.7	4.6	(Cl) 13.5	acetic anhydride	209–210	~243 (20.4) 428 (15.7)
					50.0	4.7	(Cl) 13.5			~266 (17.4) 453 (15 4)
										313 (31.2)
22	D-6	C	78	$C_{22}H_{24}Cl_2N_2O_6S$	48.3	4.4	5.1	acetic anhydride	249–250	267 (17.4) 400 (17.2)
					48.3	4.2	4.9			303 (27.4) 520 (11.9)
23	A-7	C	90	$C_{29}H_{30}Cl_2N_2O_{11}$	50.6	4.9	4.5	acetonitrile	235–236	266 (14.3) 407 (36.2)
					50.4	4.6	4.2			310 (19.0) 479 (28.0)
24	B-6	D	84	$C_{27}H_{24}ClNO_5$	67.8	5.1	2.9	acetonitrile	260–261	255 (14.4) 432 (40.4)
					67.4	5.2	3.2			340 (14.4) 453 (40.0)
25	B-7	D	93	$C_{23}H_{22}ClNO_5$	64.6	5.2	3.3	acetonitrile	272–273	253 (10.2) 423 (42.6)
					64.5	5.2	3.1			280 (8.8) 445 (33.3)
										335 (15.6)
26	A-8	D	66	$C_{27}H_{24}ClNO_5$	67.8	5.1	2.9	acetonitrile	255–256	245 (18.6)
					67.8	5.2	2.7			318 (26.4)
										500 (16.3)
27	A-9	D	50	$C_{23}H_{22}ClNO_5$	64.6	5.2	3.3	pyridine +	229–230	275 (101.0)
					64.5	5.3	3.1	methyl alcohol		465 (20.0)
28	D-7	D	51	$C_{23}H_{22}ClNO_5$	66.4	4.9	3.1	acetonitrile	241–242	238 (22.0)
					66.4	4.6	2.9			320 (14.2)
										445 (35.4)
29	D-8	D	95	$C_{21}H_{20}ClNO_5$	62.8	5.0	3.5	acetonitrile	226–227	238 (19.0)
					62.8	5.1	3.2			317 (16.5)
										430 (36.7)

[a] The structures are given in Chart I, and to aid in finding these structures they have been designated in the tables by a capital letter to indicate the heterocyclic nucleus followed by a number to give the position of the compound in the listings below these nuclei. [b] Prepared from 2-methyl-4,6-diphenylpyrylium perchlorate and N-methylacetamide by procedure A.

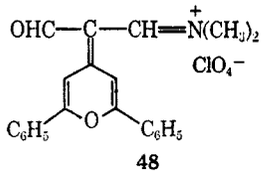
TABLE II

HYDROLYSIS PRODUCTS OF IMINIUM SALTS

Compd number	Structure	Method of preparation	Yield, %	Empirical formula	Anal. Calcd, % C	Anal. Calcd, % H	Anal. Found, % N or S	Solvent of recrystallization	Mp, °C	Absorption spectra in acetonitrile, λ,mμ (ε × 10⁻³)	
30	A-10	H	82	$C_{19}H_{14}O_2$	83.2	5.1		ligroin	125–126	224 (13.5)	327 (10.0)
					83.4	5.3		(bp 63–75°)		286 (33.4)	445 (9.7)
31	A-11	H	52	$C_{20}H_{16}O_2$	83.3	5.6		ethyl alcohol	170–171	228 (15.2)	340 (13.4)
					83.4	5.8				283 (30.2)	4
32[a]	C-4	H and I	62; 74	$C_{22}H_{18}O_2$	84.0	5.8		benzene +	165–166	227 (13.9)	352 (8.0)
					83.7	5.5		ligroin		282 (26.2)	443 (9.9)
								(bp 63–75°)		340 (9.9)	
33	B-8	H and I	90; 87	$C_{19}H_{14}O_2$	83.2	5.1		ethyl ether	89–90	241 (11.8)	298 (18.0)
					83.3	5.4				272 (12.5)	370 (26.0)
34	D-9	H	80	$C_{17}H_{12}O_2$	82.2	4.9		methyl alcohol	110–111	244 (21.8)	
					81.9	4.8				295 (15.7)	
										374 (21.4)	
35	D-10	H	81	$C_{17}H_{12}OS$	77.2	4.6	(S) 12.1	methyl alcohol	89–90	255 (27.2)	
					77.7	4.5	(S) 11.9			299 (13.4)	
										401 (19.7)	
36	E-2	J	74	$C_{18}H_{14}O_2$	82.4	5.4		methyl alcohol	172–173	257 (21.8)	342 (13.2)
					82.3	5.3				267 (20.8)	357 (10.8)
										278 (20.4)	404 (14.0)
										327 (10.4)	419 (16.5)
											438 (12.9)
37	A-12	H	44	$C_{20}H_{16}O_2$	83.3	5.6		ethyl alcohol	115–117	...	
					83.2	5.8					
38	B-9	H	69	$C_{20}H_{16}O_2$	83.3	5.6		ethyl alcohol	109–110	230 (12.2)	297 (18.0)
					83.0	5.9				270 (12.9)	375 (24.7)
39	C-5	I	64	$C_{23}H_{20}O_2$	84.1	6.2		ethyl alcohol	142–143	...	
					84.0	6.4					
40	D-11	I	78	$C_{18}H_{14}O_2$	82.4	5.4		methyl alcohol	111–112	243 (25.4)	
					82.3	5.6				296 (15.3)	
										380 (18.2)	
41	B-10	I	51	$C_{21}H_{16}O_2$	84.0	5.4		acetonitrile	165–166	245 (13.9)	
					83.9	5.9				302 (13.9)	
										421 (39.2)	
42	C-6	I	63	$C_{24}H_{20}O_2$	84.7	5.9		acetonitrile	196–197	242 (17.6)	365 (15.0)
					84.5	6.2				255 (18.3)	384 (15.8)
										270 (19.8)	470 (13.6)
										~345 (12.8)	~510 (11.6)
43	F-2	I	67	$C_{23}H_{16}O_2$	85.2	5.0		acetonitrile	171–172	...	
					84.9	5.1					
44	B-11	K	88	$C_{20}H_{14}O_3$	79.5	4.7		acetonitrile	234–235	...	
					79.6	4.9					
45[b]	B-12	K	96	$C_{25}H_{18}O_2$	85.7	5.2		ethyl alcohol	158–159	222 (19.4)	305 (16.4)
					85.4	5.5				247 (17.9)	410 (33.4)
46[c]	D-12	K	97	$C_{23}H_{16}O_2$	85.2	5.0		ethyl alcohol	129–130	250 (22.5)	
					85.0	4.9				295 (15.9)	
										405 (26.4)	
47	D-13	L	24	$C_{20}H_{13}ClNO_6$	59.5	4.5		acetonitrile	234–235	...	
					59.6	4.4					
48	B-13	J	31	$C_{22}H_{20}ClNO_6$	61.5	4.7	3.3	acetic acid	224–225	...	
					61.2	5.0	3.3				
49	G-1	see Experimental Section		$C_{21}H_{19}NO$	83.7	6.4	4.7	isopropyl alcohol	145–146	...	
					83.6	6.4	4.7				
50	G-2	see Experimental Section		$C_{20}H_{16}O_2$	83.3	5.6		ligroin	93–94	...	
					83.3	5.8		(bp 63–75°)			
53	G-3	see Experimental Section		$C_{23}H_{21}NO_2$	80.4	6.2	4.1	butyl alcohol	152	...	
					80.2	6.2	4.0				
54	G-4	see Experimental Section		$C_{24}H_{23}NO$	84.5	6.8	4.1	ligroin	110	...	
					84.5	6.6	4.2	(bp 63–75°)			

[a] H. D. Kirmer and R. Wizinger, *Helv. Chim. Acta*, **44**, 1766 (1961). [b] H. Strzelecka, *Ann. Chim.*, 201 (1966). [c] J. A. VanAllan, G. A. Reynolds, and T. H. Regan, *J. Org. Chem.*, **32**, 1897 (1967).

aqueous pyridine rather than methanolic potassium hydroxide, only one of the iminium groups was hydrolyzed, and compound **48** was obtained.



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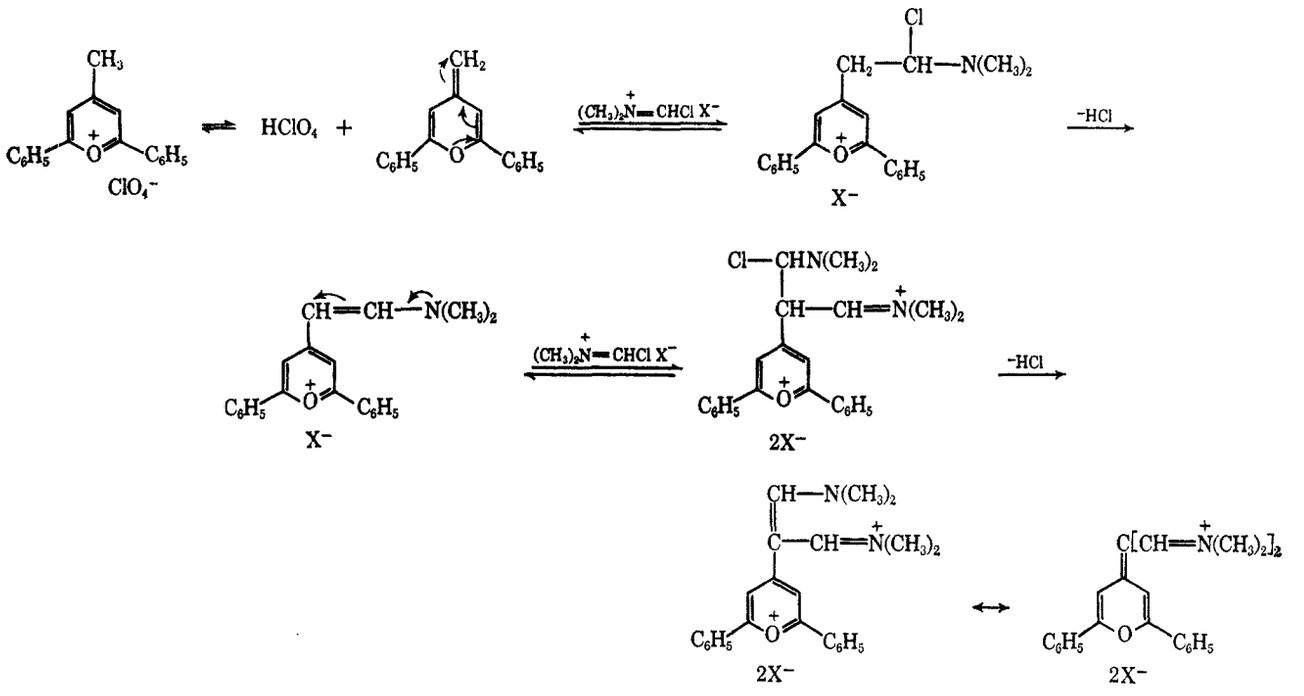
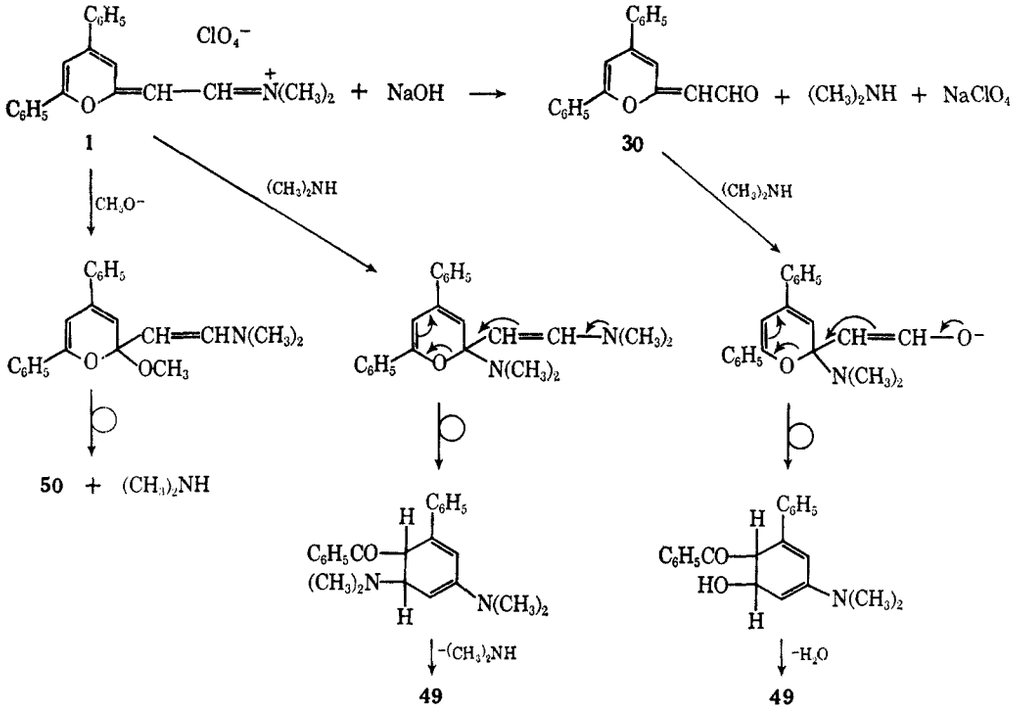
Alkaline hydrolysis of the iminium salt **1** gave rise to a mixture of products, and the reaction conditions were found to change the reaction path. The methods which were used for the hydrolysis of **1** are (a) a mixture of **1**, 2% aqueous sodium hydroxide, and ether was stirred for 24 hr; (b) a mixture of **1**, 2% sodium hydroxide, and chloroform was stirred for 3 hr; (c) a solution of **1** in 5% methanolic potassium hydroxide was refluxed for 1 hr. On the basis of the other hydrolyses described in this paper, it was expected that the product would be the aldehyde **30** (Scheme II). Although **30** was the major product from procedure a, it was a minor product from procedure b and was not obtained by procedure c. The principal product isolated by procedure b was 4-dimethylamino-2-phenylbenzophenone (**49**), and procedure c gave a mixture of **49** and 4-methoxy-2-phenylbenzophenone (**50**). The structural assignments for **49** and **50** were made on the basis of the elemental analysis and nmr, ultraviolet, infrared, and mass spectra.

SCHEME I



SCHEME II



The absorption maxima for **49** and **50** are compared with those of 4-dimethylaminobenzophenone (**51**) and 4-methoxybenzophenone (**52**) in Table III; the similarity of the spectra of the related compounds is apparent. The carbonyl stretching vibrations for these compounds are also recorded in Table III.

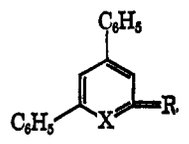
The mass spectrometric analyses of **49** and **50** were consistent with the proposed structures, and some of the major fragmentations are (**49**) M (*m/e*) 301, *m/e* 224, 180, 152; (**50**) M (*m/e*) 288, *m/e* 211, 168, 140, 139 105.

The nmr spectra of **49** and **50** demonstrated that a 1,2,4-trisubstituted phenyl ring was present in these compounds. The 100-MHz spectrum of **49** in benzene-d_6 has absorption at τ 7.49 (s, 6 H, NMe_2) and from τ 3.6 to 2.5 (complex m, 13 H, ArH). The substitution pattern on the central ring is clearly seen, however, from the typical ABX pattern characteristic of

CHART I

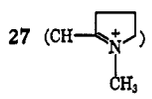
STRUCTURES OF COMPOUNDS IN TABLES II AND III

A



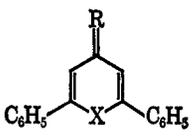
R

1 ($CHCH{=}N^+(CH_3)_2$)
2 ($C(CH_3)CH{=}N^+(CH_3)_2$)
8 ($CHCH{=}N^+(CH_3)COCH_3$)
9 ($CHC(CH_3){=}N^+(CH_3)_2$)
13 ($CHCH{=}CHCH{=}N^+(C_2H_5)_2$)
19 ($C[CH{=}N^+(CH_3)_2]_2$)
23 (*p*-methoxy in both phenyls; R as in 19)
26 ($CHC(C_6H_5){=}N^+(CH_3)_2$)

27 

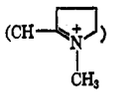
30 (CHCHO)
31 ($C(CH_3)CHO$)
37 ($CHCOCH_3$)

B



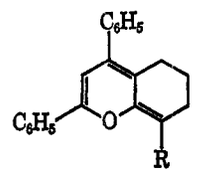
R

4 ($CHCH{=}N^+(CH_3)_2$)
10 ($CHC(CH_3){=}N^+(CH_3)_2$)
14 ($CHCH{=}CHCH{=}N^+(C_2H_5)_2$)
15 (X = S; R as in 14)
20 ($C[CH{=}N^+(CH_3)_2]_2$)
24 ($CHC(C_6H_5){=}N^+(CH_3)_2$)

25 

33 (CHCHO)
38 ($CHCOCH_3$)
41 ($CHCH{=}CHCHO$)
44 ($C[CHO]_2$)
45 ($CHCOC_6H_5$)
48 ($C(CHO)CH{=}N^+(CH_3)_2$)

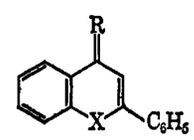
C



R

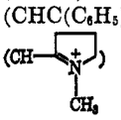
3 ($CH{=}N^+(CH_3)_2$)
11 ($C(CH_3){=}N^+(CH_3)_2$)
16 ($CH{=}CHCH{=}N^+(C_2H_5)_2$)
32 (CHO)
39 ($COCH_3$)
42 ($CH{=}CHCHO$)

D



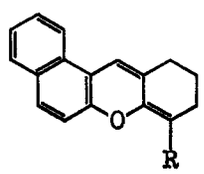
R

5 ($CHCH{=}N^+(CH_3)_2$)
6 (X = S; R as in 5)
12 ($CHC(CH_3){=}N^+(CH_3)_2$)
17 (4′-chloro; R is $CHCH{=}CHCH{=}N^+(C_2H_5)_2$)
21 ($C[CH{=}N^+(CH_3)_2]_2$)
22 (X = S; R as in 21)
28 ($CHC(C_6H_5){=}N^+(CH_3)_2$)

29 

34 (CHCHO)
35 (X = S; R as in 34)
40 ($CHCOCH_3$)
46 ($CHCOC_6H_5$)
47 ($C(CHO)CH{=}N^+(CH_3)_2$)

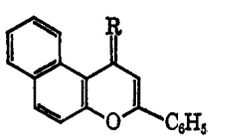
E



R

7 ($CH{=}N^+(CH_3)_2$)
36 (CHO)

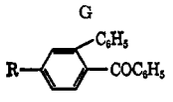
F



R

18 ($CHCH{=}CHCH{=}N^+(C_2H_5)_2$)
43 ($CHCH{=}CHCHO$)

G



R

49 ($N(CH_3)_2$)
50 (OCH_3)

53 

54 

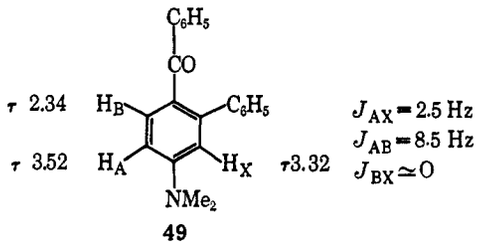
1,2,4-trisubstituted benzenes. Compound **50** has a singlet at τ 6.76 (3 H, OCH_3) and a complex multiplet from τ 3.4 to 2.2 (13 H, ArH). As expected for this compound, the signals for the protons *ortho* to the methoxy group are at lower field than the analogous protons for **49** and the H_x signal falls on the side of a complex absorption. The assignments for the protons of **50** are H_A, τ 3.28; H_B, τ 2.54; H_X, τ 3.09; J_{AB} = 8.5 Hz; J_{AX} = 2.5 Hz; $J_{BX} \simeq 0$.

TABLE III

ABSORPTION MAXIMA OF BENZOPHENONE DERIVATIVES

Compd	λ_{max}, mμ	ε × 10^{-3}	Solvent	CO vibration, μ
49	241	25.6	acetonitrile	6.08
	346	11.1		
51[a]	247	15.7	alcohol	6.1
	355	20.6		
50	245	24.3	acetonitrile	6.05
	285	7.8		
	249	9.0		
52[b]	283	16.0	alcohol	6.05
	288	16.55		

[a] H. Szmant and C. McGinnis, *J. Amer. Chem. Soc.*, **74**, 241 (1952). [b] E. Moriconi, W. O'Connor, and W. Forbes, *ibid.*, **82**, 5454 (1960).



49

Scheme II shows a reaction path which accounts for the formation of **30**, **49**, and **50** from the hydrolysis of **1**.

To test the proposed reaction scheme, **1** and dimethylamine were heated in alcohol for a short time and **49** was isolated in high yield. The same results were obtained when the aldehyde **30** was treated with dimethylamine. The substitution of other secondary amines for dimethylamine in these reactions also gave aminobenzophenone derivatives. For example, **1** and morpholine gave 4-morpholino-2-phenylbenzophenone (**53**), and **1** and piperidine gave 4-piperidino-2-phenylbenzophenone (**54**). The reaction of **1** with sodium methoxide in methanol gave **50** and a small amount of **49**. The reaction of **1** with 5% potassium hydroxide in methanol gave about 75% **49** and 25% **50**, and, when 25% methanolic potassium hydroxide was used, approximately equal amounts of **49** and **50** were formed. We were unable to isolate 4-hydroxy-2-phenylbenzophenone from any of our experiments. This result may be due to the low nucleophilicity of the hydroxide ion or because attack of hydroxide at the 2 position of the pyran ring is reversible. The results described above are consistent with nucleophilic attack of secondary amine or methoxide ion at the 2 position of the pyran ring followed by rearrangement as shown in Scheme II. The dimethylamine, which is necessary for the formation of **49**, is produced by the hydrolysis of the iminium bond and also from the final aromatization step.

Probably the formation of the aldehyde **30** by procedure a is the result of the poor solubility of **30** in ether, which prevents subsequent reaction to form rearranged products.

Experimental Section

The methods of preparation of the various classes of compounds are described as general procedures. The compounds are listed in Tables I and II along with the methods of preparation and some physical properties.

Preparation of Monoiminium Salts. Procedure A.—A mixture of 5 g of alkylpyrylium perchlorate, 3 ml of N,N-dimethylformamide, and 100 parts of acetic anhydride was refluxed for 15 min. The mixture was cooled, and if no product separated, ether was added to precipitate the crude product, which was collected and recrystallized.

Procedure B.—A mixture of 0.02 mol of alkylpyrylium salt, 0.02 mol of N,N-dimethylthioacetamide, and 30 ml of acetic anhydride was refluxed for 30 min and chilled, and the product was collected and recrystallized.

Procedure C.—A solution of the Vilsmeier complex was prepared from 2 ml of phosphorous oxychloride and 10 ml of cold N,N-dimethylformamide, 0.01 mol of the alkylpyrylium perchlorate was added, and the solution was heated for 30 min on a steam bath. The reaction mixture was poured onto ice and the solid was collected.

Procedure D.—This procedure was the same as C, except that N,N-dimethylacetamide, N,N-dimethylbenzamide, and N-methylpyrrolidinone were used rather than dimethylformamide.

Procedure E.—A mixture of 2 g of alkylpyrylium perchlorate, 2 ml of diethylaminoacrolein, and 50 ml of acetic anhydride was stirred at room temperature for 2 hr. It was then diluted with ether and chilled, and the solid was collected.

Procedure F.—A mixture of 0.01 mol of active methyl compound, 0.012 mol of N,N-diethyl-N-(1-methoxy-1-propen-3-ylidene)-ammonium methylsulfate,[4] 2 ml of N,N-diisopropylethylamine, and 25 ml of alcohol was heated on a steam bath for 15 min and chilled, and the solid was collected.

Preparation of Bisiminium Salts. Procedure G.—This procedure was the same as C, except that the amount of N,N-dimethylformamide was doubled.

Preparation of Monoaldehydes. Procedure H.—A mixture of 0.01 mol of the monoiminium salt, 75 ml of 2% aqueous sodium hydroxide, and 75 ml of ether was stirred for 24 hr. The ether phase was separated. In some cases the aldehyde was sparingly soluble in ether and additional ether was added. The ether extracts were dried, the solvent was removed, and the residue was recrystallized.

Procedure I.—A mixture of 0.01 mol of monoiminium salt and 50 ml of 5% methanolic potassium hydroxide was heated on a steam bath for 0.5 hr and chilled, and the solid was collected.

Procedure J.—A mixture of 0.01 mol of iminium salt, 25 ml of pyridine, and 2 ml of water was refluxed for 1 hr, cooled, and diluted with water, and the solid which separated was collected.

Preparation of Bisaldehydes. Procedure K.—Procedure H was duplicated with a bisiminium salt.

Procedure L.—Procedure I was employed with a bisiminium salt.

4-[3-(4H-Flaven-4-ylidene)-2-methyl-1-propenyl]flavylium Perchlorate.—A mixture of 3 g of 4-methylflavylium perchlorate, 3 ml of N,N-dimethylacetamide, and 25 ml of acetic anhydride was refluxed for 0.5 hr and chilled, and the dark solid was collected and recrystallized from acetonitrile to give 2.4 g of the cyanine dye.

Anal. Calcd for $C_{32}H_{23}ClO_6$: C, 71.3; H, 4.3; Cl, 6.6. Found: C, 71.6; H, 4.3; Cl, 6.6.

4-Dimethylamino-2-phenylbenzophenone (49).—(a) A mixture of 2 g of the iminium salt **1**, 50 ml of chloroform, and 50 ml of 2% aqueous sodium hydroxide was stirred for 3 hr. The organic phase was separated and the solvent was removed. Analysis of the residue by vpc showed that it consisted of 62% **49** and 38% aldehyde **30**. These two compounds were readily separated by preparative vpc, or they could be fractionally crystallized from isopropyl alcohol to give **49**, and the alcohol-soluble fraction was then crystallized from ligroin (bp 63–75°) to give **30**.

(b) A mixture of 1 g of **1** or 1 g of the aldehyde **30**, 5 ml of 25% aqueous dimethylamine, and 50 ml of alcohol was heated on a steam bath for 0.5 hr and diluted with water, and the solid was collected and recrystallized to give **49** in 85% yield (from **1**) and 88% yield (from **30**).

4-Methoxy-2-phenylbenzophenone (50).—(a) A mixture of 12 g of **1** and 100 ml of 5% methanolic potassium hydroxide was heated on a steam bath for 1 hr and poured into water, and the solid was extracted into benzene. The benzene extract was dried ($MgSO_4$) and the solvent removed. The residue as analyzed by vpc consisted of 75% **49** and 25% **50**. Distillation of the residue followed by crystallization of the distillation fractions did not completely separate **49** and **50**. The two products were separated by preparative vpc, yielding 5.1 g of **49** and 1 g of **50**.

When this procedure was repeated using 100 ml of 25% methanolic potassium hydroxide, the reaction mixture consisted of approximately equal parts of **49** and **50**, as shown by vpc.

(b) A mixture of 2 g of **1**, 4 g of sodium methoxide, and 75 ml of methanol was heated on the steam bath for 1 hr, cooled, and diluted with water, and the sticky solid was collected and recrystallized to give **50** in 87% yield.

4-Morpholino-2-phenylbenzophenone (53).—A mixture of 2 g of **1**, 3 ml of morpholine, and 25 ml of alcohol was heated on a steam bath for 15 min and poured into water, and the solid was collected and recrystallized to give 1.2 g of **53**.

4-Piperidino-2-phenylbenzophenone (54).—This compound was prepared as described for **53**, piperidine being substituted for morpholine; yield 1.3 g.

Registry No.—**1**, 20439-71-8; **2**, 20439-72-9; **3**, 20439-73-0; **4**, 20439-74-1; **5**, 20439-75-2; **6**, 20420-95-5; **7**, 20439-76-3; **8**, 20439-77-4; **9**, 20439-78-5; **10**, 20439-79-6; **11**, 20439-80-9; **12**, 20439-81-0; **13**, 17203-20-2; **14**, 17203-19-9; **15**, 17203-24-6; **16**, 17203-21-3; **17**, 17203-22-4; **18**, 17203-23-5; **19**, 20439-85-4; **20**, 20439-86-5; **21**, 20439-87-6; **22**, 20439-88-7; **23**, 20420-94-4; **24**, 20399-80-8; **25**, 20399-81-9; **26**, 20399-82-0; **27**, 20399-83-1; **28**, 20399-84-2; **29**, 20399-85-3; **30**, 20399-86-4; **31**, 20399-87-5; **32**, 20399-88-6; **33**, 20399-89-7; **34**, 20399-90-0; **35**, 20399-91-1; **36**, 20399-92-2; **37**, 20399-93-3; **38**, 1914-17-6; **39**, 20399-95-5; **40**, 20399-96-6; **41**, 17203-26-8; **42**, 17202-98-1; **43**, 17202-97-0; **44**, 20400-00-4; **45**, 1914-13-2; **46**, 10385-47-4; **47**, 20400-03-7; **48**, 20400-04-8; **49**, 20400-05-9; **50**, 20400-06-0; **53**, 20400-07-1; **54**, 20400-08-2.

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