

Pyranilidene Iminium Salts II. Iminium Salts Derived from Pyrones, Dialkylamides and Phosphorus Oxychloride

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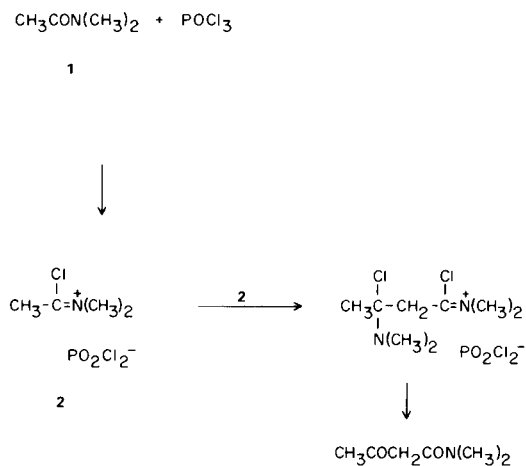
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N,N-Dialkylamides, pyrones, and phosphorus oxychloride react to give pyranilidene chloroiminium salts. The chlorine atom of these salts is readily displaced by nucleophiles to yield a variety of pyranilidene derivatives.

The condensation of certain alkyl substituted pyrylium salts with *N,N*-dimethylformamide, *N,N*-dialkylamides, and *N,N*-dialkylthioamides to give pyranilidene iminium salts was described recently (1). The present paper describes the preparation of some chloroiminium salts by the reaction of *N,N*-dialkylamides and pyrones in the presence of phosphorus oxychloride.

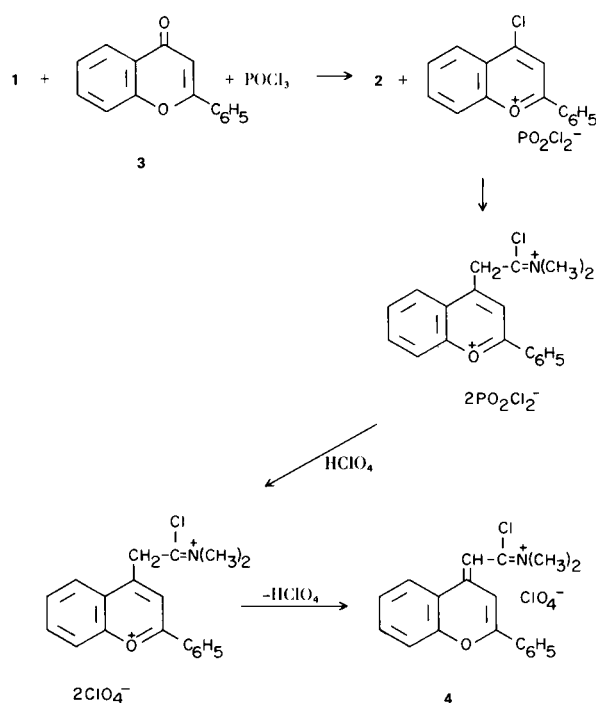
It has been reported (2) that certain *N,N*-dialkylamides yield self-condensation products in the presence of acid halides such as phosphorus oxychloride. A typical reaction of this type is shown in Scheme I. We have found

SCHEME I



that the methyl group of complexes such as **2** will condense with very reactive electrophiles to give mixed condensation products. For example, a mixture of **1**, flavone (**3**), and phosphorus oxychloride gives the iminium salt **4** (Scheme II). In this example, the electrophilic 4-chloro-

SCHEME II



flavylum salt, which is presumably formed from **3** and phosphorus oxychloride, condenses with the methyl group of **2**.

The reaction shown in Scheme II was repeated with 2,6-diphenyl-4-pyrone (**5**) in place of **3** to give a product derived from two equivalents of **5** and one equivalent of **1** (Scheme III). It is not known whether the difference in behavior of **3** and **5** is due to steric factors or to a difference in electrophilicity of the chloropyrylium and chloroflavylum intermediates.

TABLE I

Pyran Derivatives

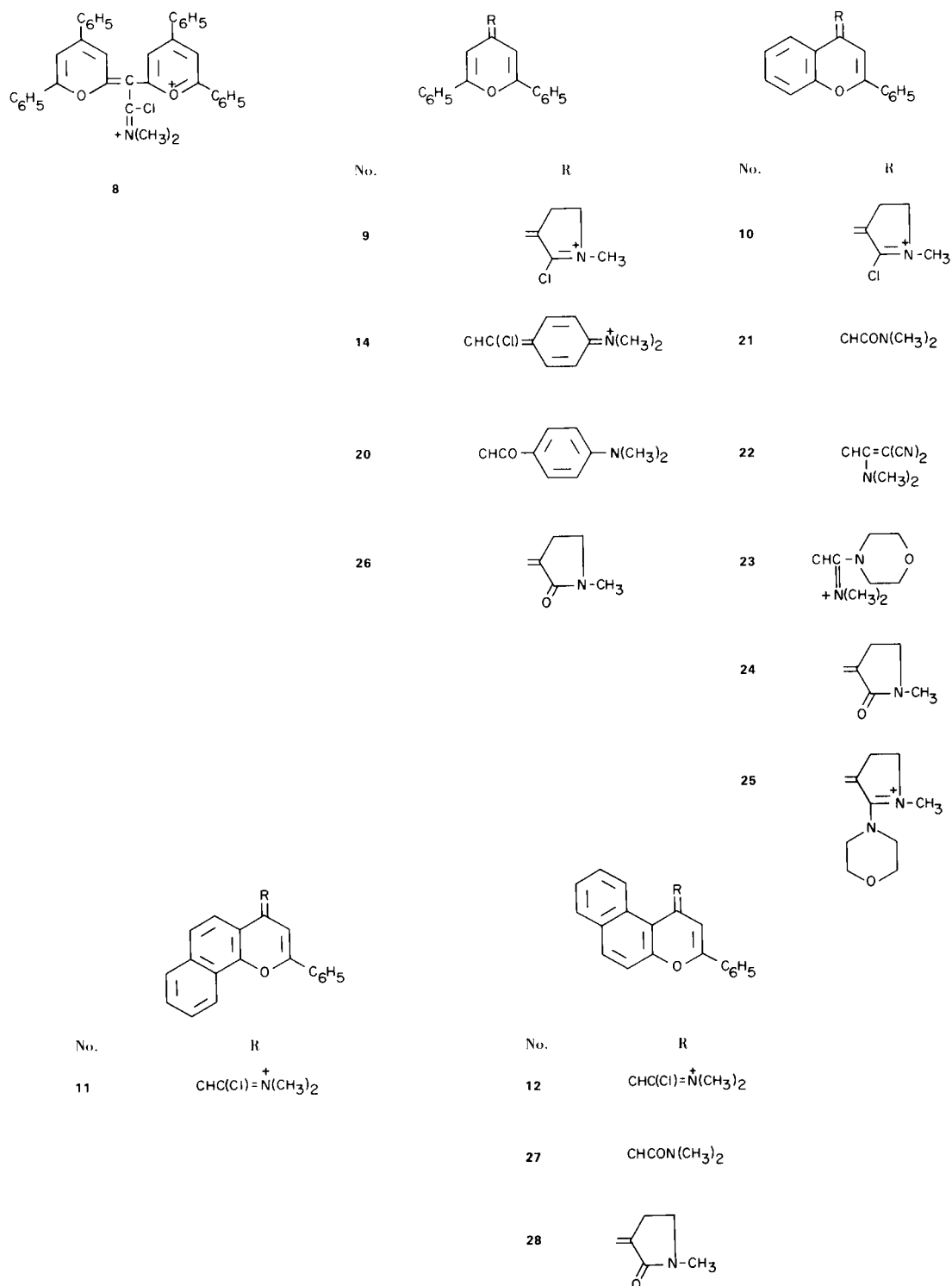
Structure (a)	Compound number	Method of preparation	Yield, %	Empirical formula	C	H	N (Cl)	Solvent of recrystallization (b)	m.p. °C	Absorption spectra in acetonitrile λ , m μ ($\epsilon \times 10^{-3}$)
Text	4	A	76	C ₁₉ H ₁₇ Cl ₂ NO ₅	55.5 55.4	4.1 3.9	(Cl) 17.3 (Cl) 17.0	a	198-199	242 (19.2) ~268 (8.0) 340 (12.4) 445 (37.2) 461 (37.3)
Text	7	A	61	C ₃₈ H ₃₀ Cl ₃ NO ₁₀	59.4 59.2	3.9 4.2	(Cl) 13.8 (Cl) 13.8	a	275 (explodes)	232 (26.2) 275 (13.0) 409 (22.7) 443 (18.2) 532 (10.5)
Chart I	8	A	52	C ₃₈ H ₃₀ Cl ₃ NO ₁₀	59.4 59.7	3.9 3.7	(Cl) 13.8 (Cl) 13.8	a	268 (dec.)	280 (32.5) 338 (46.7) 558 (32.8) 638 (30.0)
Chart I	9	A	21	C ₂₂ H ₁₉ Cl ₂ NO ₅	58.9 58.8	4.3 4.4	3.1 3.0	a	257-258	247 (15.2) 273 (16.1) 298 (16.0) 385 (26.4) 525 (4.0)
Chart I	10	A	71	C ₂₀ H ₁₇ Cl ₂ NO ₅	57.0 57.2	4.1 4.3	3.3 3.2	a	239-240	243 (19.8) 235 (10.0) 455 (19.2)
Chart I	11	A	88	C ₂₃ H ₁₉ Cl ₂ NO ₅	60.0 60.3	4.1 4.2	(Cl) 15.5 (Cl) 15.3	a	249-250	215 (39.0) 279 (20.8) 303 (10.6) 335 (11.2) 465 (47.9)
Chart I	12	A	57	C ₂₃ H ₁₉ Cl ₂ NO ₅	60.0 60.4	4.1 4.4	3.0 2.8	a	180-181	235 (40.0) 300 (15.2) 385 (14.4) 470 (6.4)
Chart I	14	A	61	C ₂₇ H ₂₃ Cl ₂ NO ₅	63.4 63.2	4.5 4.3	(Cl) 13.8 (Cl) 13.8	a	247-248	236 (15.6) 272 (16.6) 406 (19.8) 635 (63.8)
Text	15	C	78	C ₂₆ H ₁₉ N ₃ O	80.2 79.9	4.9 4.6	10.8 10.5	d	259-260	270 (22.6) 368 (12.4) 385 (12.7) 490 (14.8) 522 (23.9)
Text	16	B	87	C ₂₃ H ₁₉ NO ₂	80.9 80.6	5.6 5.6	4.1 4.0	a	249	272 (37.0) 328 (17.8) 360 (20.0)

Text	17	D	58	$C_{23}H_{21}ClN_2O_5$	62.7	4.8	6.4	c	228-229	270 (31.6) 365 (17.8)
Text	18	E	74	$C_{27}H_{27}ClN_2O_6$	63.5	5.3	5.5	d	289-290	277 (21.4) 328 (14.1) 385 (15.5)
Text	19	E	84	$C_{25}H_{21}NO_3$	78.2	5.5	3.6	n	194-195	258 (35.8) 350 (19.8)
Chart I	20	B	45	$C_{27}H_{23}NO_2$	82.4	5.8	3.6	e	180-182	248 (20.9) 300 (14.0) 420 (11.4)
Chart I	21	B	53	$C_{19}H_{17}NO_2$	78.4	5.8	4.8	l	132-133	240 (28.4) 283 (19.2) 360 (19.4)
Chart I	22	C	64	$C_{22}H_{17}N_3O$	78.0	5.0	12.4	a	289-290	290 (9.0) 358 (6.2) 310 (9.3) 523 (69.0)
Chart I	23	E	85	$C_{23}H_{25}ClN_2O_6$	60.0	5.4	6.1	a	254-255	233 (25.2) 295 (16.8) 385 (20.7)
Chart I	24	B	58	$C_{20}H_{17}NO_2$	79.2	5.7	4.6	e	152-153	242 (31.8) 273 (35.3) 355 (22.1)
Chart I	25	E	92	$C_{24}H_{25}ClN_2O_6$	61.0	5.2	6.0	a	199-200	239 (23.1) 300 (15.4) 410 (20.6)
Chart I	26	B	48	$C_{22}H_{19}NO_2$	80.3	5.8	4.3	e	200-201	270 (22.9) 356 (26.4)
Chart I	27	B	46	$C_{23}H_{19}NO_2$	80.9	5.6	4.1	l	127-128	256 (36.2) 298 (20.6) 363 (13.4)
Chart I	28	B	72	$C_{24}H_{19}NO_2$	81.6	5.4	4.0	a	184-185	225 (36.9) 297 (19.9) 258 (33.8) 355 (14.5)

(a) The structures are found either in the text or in Chart I, as designated. (b) The following designations have been used for solvents: a = acetonitrile; d = *N,N*-dimethylformamide; n = nitromethane; e = ethyl alcohol; l = ligroin (b.p. 100-115°); c = acetic acid.

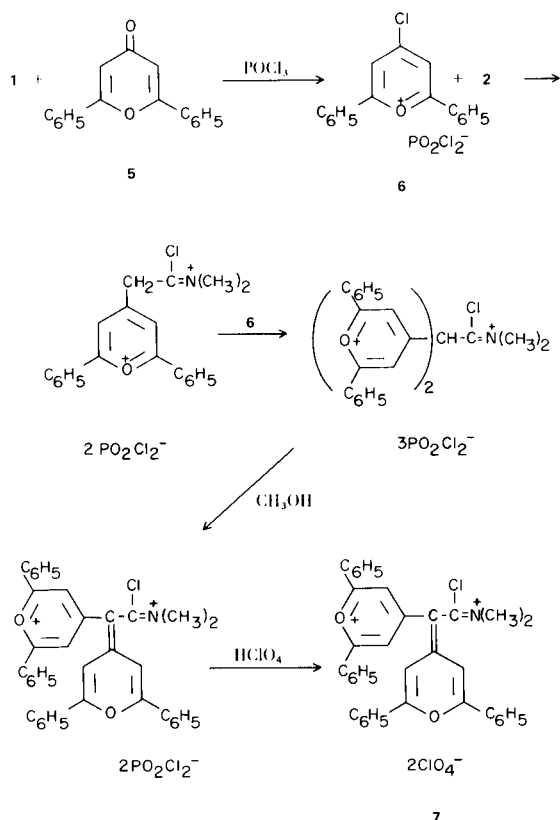
CHART I

Structures of Compounds in Table I (a)



(a) For examples that are salts, only the structure for the cation is given. In all cases the anion is perchlorate and is not shown.

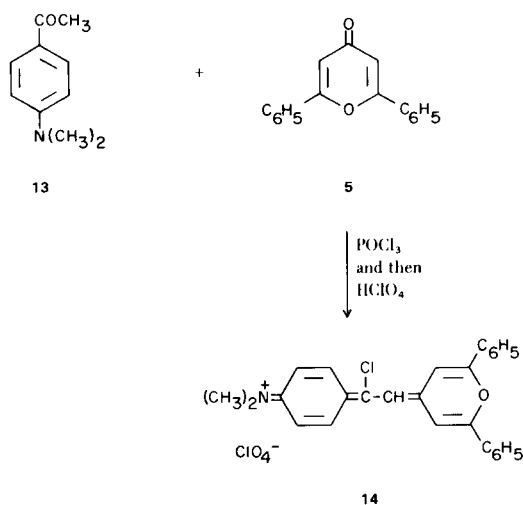
SCHEME III



The products (**4**, **7**, **8-12**) which were prepared by the reaction of *N,N*-dialkylamides, pyrone derivatives, and phosphorus oxychloride are listed in Table I.

4-Dimethylaminoacetophenone (**13**), which can be considered to be a vinylogous dialkylamide, also reacts with pyrones in the presence of phosphorus oxychloride to give iminium salt (**14**) (Scheme IV).

SCHEME IV



The chloroiminium salts described in this paper react with nucleophilic reagents as illustrated in Scheme V for **11**. Other examples of products obtained from chloroiminium salts and nucleophiles (compounds **20-28**) are recorded in Table I.

The electronic absorption maxima for all compounds are included in Table I. The maxima for the chloroiminium salts correspond to those of previously reported (1) iminium salts, as illustrated by a comparison of the maxima of **4** (see Table I) and A.

	λ	$(\epsilon \times 10^{-3})$
	241	(19.3)
	268	(8.3)
	320	(14.2)
	428	(39.5)
	450	(31.3)

It is obvious that the preparation of chloroiminium salts could be extended to include other pyrones and amides, and that these very reactive salts would react with a variety of nucleophiles.

EXPERIMENTAL

The methods used for the preparation of the compounds listed in Table I are described as general procedures.

Preparation of Chloroiminium Salts.

Procedure A.

A mixture of 0.025 mole of *N,N*-dimethylacetamide or *N*-methylpyrrolidinone and 0.02 mole of the pyrone in 10 ml. of phosphorus oxychloride was heated on a steam bath for 2 hours. The excess phosphorus oxychloride was evaporated under reduced pressure, the residue was dissolved in methanol, 3 ml. of 70% perchloric acid was added to the solution, and after chilling, the solid which separated was collected and recrystallized.

Reactions of Chloroiminium Salts.

Hydrolysis, B.

A mixture of 0.01 mole of the chloroiminium salt, 2 g. of potassium acetate, and 50 ml. of methyl alcohol was heated on a steam bath for 2 hours, diluted with 50 ml. of water, and the solid was collected.

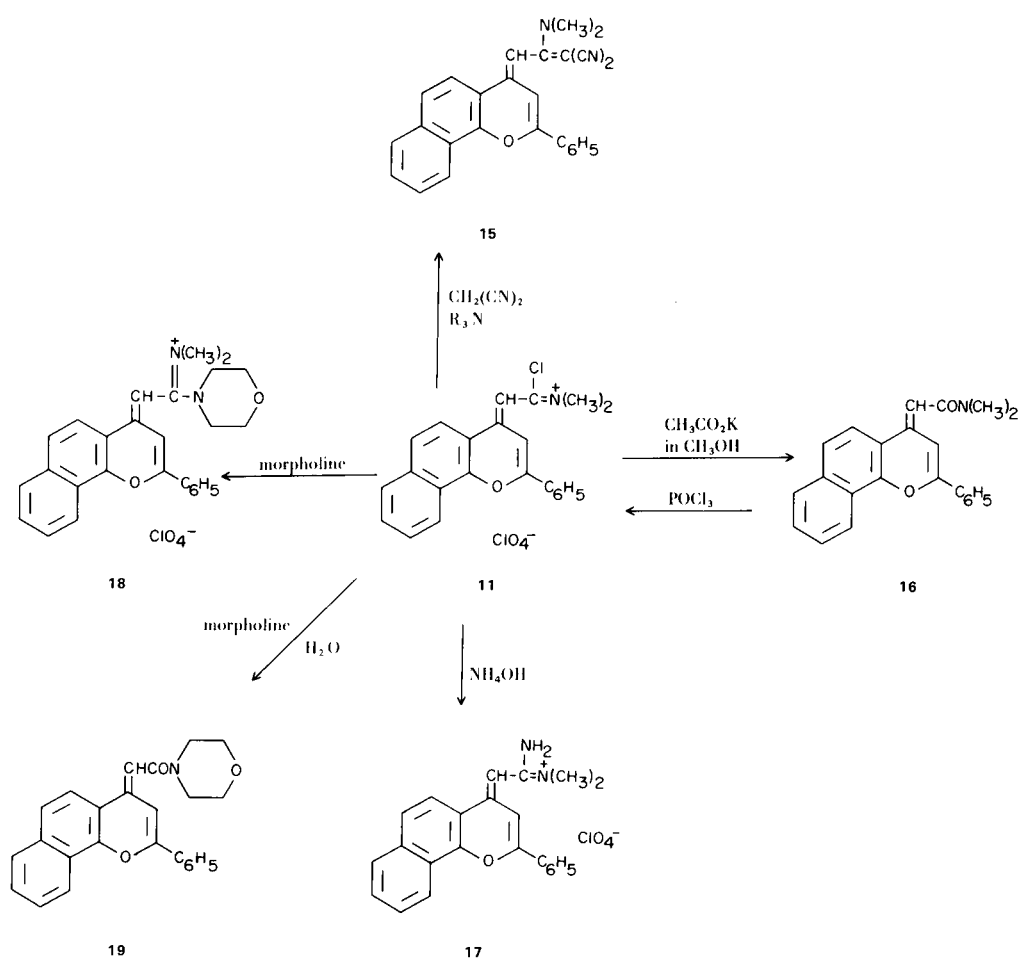
Reaction with Malononitrile, C.

A mixture of 0.01 mole of the chloroiminium salt, 3 g. of malononitrile, 4 ml. of diisopropylethylamine, and 50 ml. of acetonitrile was heated under reflux for 2 hours, chilled, and the solid was collected.

Reaction with Ammonia, D.

A mixture of 0.01 mole of the chloroiminium salt, 12 ml. of pyridine, and 6 ml. of concentrated ammonium hydroxide was heated under reflux for 2 hours, diluted with water, and the

SCHEME V



solid was collected.

Reaction with Morpholine, E.

A solution of 0.01 mole of the chloroiminium salt in 25 ml. of morpholine was heated on a steam bath for 2 hours, diluted with alcohol, and the solid was collected.

Compound **19** was obtained when the reaction was carried out in the presence of 2 ml. of water.

REFERENCES

- (1) G. A. Reynolds and J. A. VanAllan, *J. Org. Chem.*, **34**, 2736 (1969).
- (2) H. Eilingsfeld, M. Seefleder and H. Weidinger, *Angew. Chem.*, **72**, 836 (1960).

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