

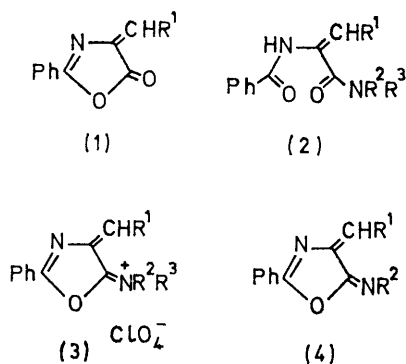
Synthesis of *N*-(4-Arylmethylene- Δ^2 -oxazolin-5-ylidene)ammonium Salts and their Conversion into 5-Imino- Δ^2 -oxazolines and 1,3-Diazafulvenes

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Treatment of seven secondary or tertiary amides of α -benzamidocinnamic acids with acetic anhydride-perchloric acid gave *N*-(4-arylmethylene-2-phenyl- Δ^2 -oxazolin-5-ylidene)ammonium perchlorates. The *N*-monosubstituted iminium salts were deprotonated to yield the corresponding 4-arylmethylene-5-imino- Δ^2 -oxazolines; successive treatment of two *NN*-disubstituted iminium perchlorates with ammonia and sodium hydroxide produced novel 1,3-diazafulvenes (4-arylmethylene-5-dimethylamino-2-phenyl-4*H*-imidazoles).

A VARIETY of cyclic oxygen-containing cations is produced by the action of acetic anhydride and perchloric acid on compounds of the general formula $-\text{OC}\cdot\text{X}\cdot\text{Y}\cdot\text{CO}-$: 1,3,4-oxadiazolium salts from diacylhydrazines,¹ imino-lactone salts from amic acids,² dihydrofurylidene-ammonium salts from γ -oxo-amides,³ and oxo-oxazolinium salts from α -acylamino-acids.⁴ We now report that application of the reagent to the system $-\text{OC}-\text{NH}-\overset{\text{||}}{\text{C}}-\text{CO}-\text{N}<$ results in the formation of novel heterocyclic iminium salts.

The required diamides (2) are readily prepared⁵ by the action of amines on 4-arylmethylene- Δ^2 -oxazolin-5-ones (unsaturated azlactones) (1). Treatment of α -benzamido-*NN*-dimethylcinnamamide (2a)⁶ with acetic anhydride-perchloric acid gave a high yield of the



	R ¹	R ²	R ³
a;	Ph	Me	Me
b;	<i>p</i> -MeO-C ₆ H ₄	Me	Me
c;	Ph	PhCH ₂	H
d;	Ph	Me	H
e;	Ph	Ph	H
f;	Ph	<i>p</i> -MeC ₆ H ₄	H
g;	<i>p</i> -MeO-C ₆ H ₄	Me	H

yellow salt (3a), whose structure follows from its ready hydrolysis by warm water to the benzylidenephényl-oxazolinone (1a). The i.r. spectrum of the perchlorate exhibited bands at 1681 and 1649 cm⁻¹; these are respectively assigned to the C=N⁺ and C=N vibrations by comparison with the spectrum of compound (1a) whose azomethine group absorbs at 1650 cm⁻¹. An analogous salt (3b) was obtained from the *p*-methoxy-

benzylidene derivative (2b). *N*-(α -Benzamidocinnamoyl)benzylamine (2c)⁷ was converted into the yellow *N*-monosubstituted iminium perchlorate (3c), whose structure was established by aqueous hydrolysis to the azlactone (1a). The salt is evidently protonated on the exocyclic nitrogen atom, since its electronic spectrum closely resembles that of the dimethyl analogue (3a). The *N*-monosubstituted iminium perchlorates (3d-g) were prepared from the amides (2d-g), respectively. The salts are listed in Table 1.

The benzyliminium perchlorate (3c) reacted with cold aqueous sodium carbonate to give a yellow base, C₂₃H₁₈N₂O, m.p. 128°, which was at first thought to be the geometrical isomer of the benzylidenephényl-imidazolinone (5),⁷ m.p. 144°, because the spectra of our compound [ν_{max} 1692 and 1651 cm⁻¹, λ_{max} (EtOH) 264, 362, and 377 nm] resembled those (1713 and 1640 cm⁻¹, 251, 362, and 376 nm) of the imidazolinone. However, the imino-oxazolinone structure (4c) of the new base was readily demonstrated by mild acidic hydrolysis to produce the oxazolinone (1a). The benzylimine is, to our knowledge, the first authentic representative of unsaturated 5-imino- Δ^2 -oxazolines with a substituent on the exocyclic nitrogen atom. The imine is remarkably stable; attempts to effect the isomerisation (4c) \rightarrow (5) by the action of heat, hot aqueous sodium carbonate, or boiling pyridine produced no change. Analogous yellow imino-oxazolines (4d-g) were prepared by deprotonation of the corresponding perchlorates (3d-g). All the imines were thermally stable; they exhibited an intense blue or green fluorescence in u.v. light. These compounds are listed in Table 2.

The *NN*-disubstituted iminium salt (3a) reacted with ammonia to yield an unstable oil, which on brief warming with sodium hydroxide solution was converted into an orange solid to which we assign the novel 4*H*-imidazole (1,3-diazafulvene) structure (6a) on the basis of analytical and spectral (absence of NH absorption) data. The compound was hydrolysed by hot dilute hydrochloric acid to give 4-benzylidene-2-phenylimidazolin-5-one (7a), a reaction which supports the proposed constitution. Attempts to bring about cyclo-

* G. V. Boyd, *Chem. Comm.*, 1968, 1410; G. V. Boyd and P. H. Wright, *J.C.S. Perkin I*, 1972, 909.

⁵ E. Erlenmeyer, *Ber.*, 1900, **33**, 2036.

⁶ D. K. Barnes, E., Campaigne, and R. L. Shriner, *J. Amer. Chem. Soc.*, 1948, **70**, 1769.

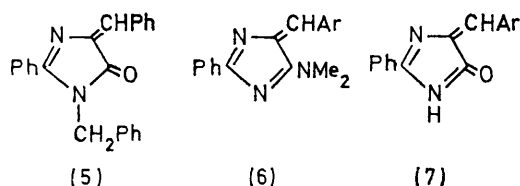
⁷ C. Gränacher and G. Gulbas, *Helv. Chim. Acta*, 1927, **10**, 819.

¹ G. V. Boyd, *Chem. Comm.*, 1967, 954; G. V. Boyd and S. R. Dando, *J. Chem. Soc. (C)*, 1970, 1397.

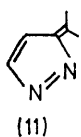
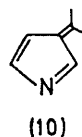
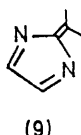
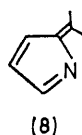
² G. V. Boyd, *Chem. Comm.*, 1969, 1147.

³ G. V. Boyd and K. Heatherington, *Chem. Comm.*, 1971, 346.

addition reactions with dimethyl acetylenedicarboxylate, *N*-phenylmaleimide, and phenyl isocyanate in boiling



a; Ar = Ph
b; Ar = *p*-MeO-C₆H₄



toluene left the starting material unchanged. The methoxy-derivative (6b) was similarly prepared from the perchlorate (3b) and hydrolysed to the imidazolinone (7b). Compounds (6a) and (6b), together

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra refer to Nujol mulls. The diamides (2a),⁸ (2c),⁷ (2d),¹¹ (2e),⁵ and (2g)⁷ were obtained according to published procedures. Compounds (2b) and (2f), prepared by heating the appropriate oxazolinone and amine in ethanolic solution, were used without purification.

N-(4-Arylmethylene-2-phenyl- Δ^2 -oxazolin-5-ylidene)-ammonium Perchlorates (3) (Table 1).—A suspension of the diamide (2) (0.05 mol) in acetic anhydride (60 ml) was cooled to 0°, and 70% perchloric acid (6.1 ml) was slowly added below 30° with vigorous stirring. A yellow solution formed which rapidly deposited the product. The mixture was kept at 0° for 1 h; the product was collected, washed with ether, and recrystallised.

Hydrolysis.—The dimethyliminium salt (3a) (0.2 g) on treatment with water (5 ml) on the steam-bath for 3 min deposited 2-phenyloxazolinone (1a) quantitatively.

4-Arylmethylene-5-imino-2-phenyl- Δ^2 -oxazolines (4) (Table 2).—The iminium perchlorate (3) (1.0 g) was stirred with a mixture of *N*-sodium carbonate (10 ml) and acetonitrile (5 ml) for 1 h. The product was filtered off and recrystallised.

Hydrolysis of 4-Benzylidene-5-benzylimino-2-phenyl- Δ^2 -oxazoline (4c).—A suspension of the imine (0.2 g) in 2*N*-hydrochloric acid (5 ml) and ethanol (5 ml) was heated on a steam-bath for 2 h. The precipitated 2-phenyloxazolinone (1a) (0.11 g, 68%) was identified by comparison with an authentic specimen.

TABLE 1

N-(4-Arylmethylene-2-phenyl- Δ^2 -oxazolin-5-ylidene)ammonium perchlorates (3)

Compound	Yield (%)	M.p. (°C) (decomp.)	Found (%)			Formula	Required (%)			λ_{\max} , ^a /nm	ν_{\max} ,/cm ⁻¹
			C	H	N		C	H	N		
(3a)	80	233—235 ^b	57.4	4.6	7.2	C ₁₈ H ₁₇ ClN ₂ O ₅	57.4	4.55	7.4	277, 389	1692, 1664
(3b)	98	248—250 ^b	56.1	4.8	6.7	C ₁₉ H ₁₉ ClN ₂ O ₆	56.1	4.7	6.9	260, ^c 283, 429	1681, 1649, 1606
(3c)	90	228—230 ^d	63.0	4.4	6.5	C ₂₃ H ₁₉ ClN ₂ O ₅	62.9	4.4	6.4	276, 394	3180, 1688, 1658
(3d)	84	242 ^d	56.3	4.1	7.75	C ₁₇ H ₁₅ ClN ₂ O ₅	56.3	4.2	7.7	<i>e</i>	3220, 1712, 1658
(3e)	87	216—217 ^d	62.5	4.0	6.6	C ₂₂ H ₁₇ ClN ₂ O ₅	62.2	4.05	6.6	<i>e</i>	3180, 1676, 1654
(3f)	89	212—215 ^d	62.8	4.3	6.45	C ₂₃ H ₁₉ ClN ₂ O ₅	62.9	4.4	6.4	<i>e</i>	3210, 1678, 1652
(3g)	89	221—224 ^d	55.1	4.4	7.0	C ₁₈ H ₁₇ ClN ₂ O ₆	55.0	4.4	7.1	259, 280, ^c 430	3220, 1701, 1644

^a In acetonitrile containing 2% of 70% perchloric acid. ^b From acetonitrile. ^c Inflection. ^d From acetic acid containing 5% of 70% perchloric acid. ^e This salt undergoes partial deprotonation in solution.

TABLE 2

4-Arylmethylene-5-imino-2-phenyl- Δ^2 -oxazolines (4)

Compound	Yield (%)	M.p. (°C)	Found (%)			Formula	Required (%)			ν_{\max} ,/cm ⁻¹
			C	H	N		C	H	N	
(4c)	99	127.5—128 ^a	81.9	5.4	8.0	C ₂₃ H ₁₈ N ₂ O	81.6	5.4	8.3	1692, 1651
(4d)	97	93—94 ^a	77.7	5.4	10.5	C ₁₇ H ₁₄ N ₂ O	77.8	5.4	10.7	1711, 1649
(4e)	95	169—170 ^b	81.4	5.0	8.4	C ₂₂ H ₁₆ N ₂ O	81.45	5.0	8.6	1679, 1650
(4f)	96	221 ^b	81.6	5.5	7.9	C ₂₃ H ₁₈ N ₂ O	81.6	5.4	8.3	1686, 1657
(4g)	87	124—125 ^a	74.1	5.5	9.2	C ₁₈ H ₁₆ N ₂ O ₂	73.95	5.5	9.6	1705, 1650

^a From aqueous ethanol. ^b From ethanol.

with the 2*H*-pyrroles (1-azafulvenes) (8),⁸ 2*H*-imidazoles (1,4-diazafulvenes) (9),^{8c,9} 3*H*-pyrroles (2-azafulvenes) (10),^{8c} and 3*H*-pyrazoles (1,2-diazafulvenes) (11),¹⁰ comprise the aza-analogues of fulvenes known to date.

⁸ (a) K. Hafner and K. Pfeiffer, *Tetrahedron Letters*, 1968, 4311; (b) C. F. Candy and R. A. Jones, *J. Chem. Soc. (B)*, 1971, 1405; (c) R. Gompper and R. Weiss, *Angew. Chem. Internat. Edn.*, 1968, 7, 296.

4-Benzylidene-5-dimethylamino-2-phenyl-4*H*-imidazole (6a).—The dimethyliminium perchlorate (3a) (5.0 g) was suspended in dry acetonitrile (15 ml), and dry ammonia was introduced until a colourless solution had formed

⁹ J. H. M. Hill, *J. Org. Chem.*, 1967, 32, 3214; W. Rohr, R. Swoboda, and H. A. Staab, *Chem. Ber.*, 1968, 101, 3491.

¹⁰ H. Bredereck, R. Sell, and F. Effenberger, *Chem. Ber.*, 1964, 97, 3407.

¹¹ A. Kjaer, *Acta Chem. Scand.*, 1953, 7, 889.

(ca. 2 h). The solution was evaporated under reduced pressure and the oily residue was dissolved in a mixture of ethanol (20 ml) and aqueous 10% sodium hydroxide (40 ml). The solution was heated to boiling on a steam-bath with intermittent shaking. After a few min an orange solid began to separate. Heating was continued for 5 min, the mixture was chilled, and the *imidazole* (1.94 g, 53%) was collected; it formed orange needles (from ethanol), m.p. 185.5°, ν_{\max} 1621, 1603sh, and 1588 cm^{-1} (Found: C, 78.5; H, 6.2; N, 15.2. $\text{C}_{18}\text{H}_{17}\text{N}_3$ requires C, 78.5; H, 6.2; N, 15.3%). The compound was recovered quantitatively after being heated with 2*N*-sodium hydroxide on a steam-bath for 3 h.

Treatment of the imidazole (0.2 g) with 2*N*-hydrochloric acid (5 ml) and ethanol (5 ml) on a steam-bath for 2 h gave

¹² E. Erlenmeyer and F. Wittenberg, *Annalen*, 1904, **337**, 294.

the yellow benzyldenephénylimidazolinone (7a) (0.18 g, 100%), m.p. 272–274° (from ethyl acetate), identified by comparison with an authentic specimen.⁵

4-*p*-Methoxybenzylidene-5-dimethylamino-2-phenyl-4*H*-imidazole (6b) (1.52 g, 40.5%) was obtained by successive treatment of the methoxybenzylidene-iminium salt (3b) (5.0 g) with ammonia and sodium hydroxide. It formed orange prisms, m.p. 151° (from ethanol), ν_{\max} 1604 and 1577 cm^{-1} (Found: C, 75.0; H, 6.4; N, 13.5. $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}$ requires C, 74.7; H, 6.3; N, 13.75%). Hydrolysis of this imidazole with aqueous ethanolic hydrochloric acid yielded 4-*p*-methoxybenzylidene-2-phenylimidazolin-5-one (7b).¹²

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