Unstable Mesoionic Oxazolium-5-oxides

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Deprotonation of seven 2,3-disubstituted 5-oxo-Δ^2-oxazolinium perchlorates yielded solutions of the corresponding mesoionic oxazolones. These compounds are too unstable to be isolated; they were trapped as stable 4-acyl derivatives by treatment with aroyl chlorides or trifluoroacetic anhydride and as pyrroles by cycloaddition to dimethyl acetylenedicarboxylate. It is shown by i.r. spectroscopy that the oxazolium-oxides decompose by a process of self-acylation to form dimeric mesoionic 4-acylaminoacyl derivatives, but in many cases the isolated products were symmetrical 1,3-di(acylamino)propan-2-ones. The relative rates of dimerisation of eight oxazolium-oxides indicate that the mesoionic system is stabilised by aryl substitution at C-2, the presence of a methyl group on the nitrogen atom, and fusion to a pyridine ring.

MESOIONIC oxazolium-5-oxides (anhydro-5-hydroxyoxazolium hydroxides) (1) have been intensively studied, notably by Huisgen and his colleagues. These ' münchnones '[1] behave as azomethine ylides [*cf.* (2)] in 1,3-dipolar cycloaddition reactions with acetylenes,[2] olefins,[3] and nitriles,[4] and carbonyl-,[5] thiocarbonyl-,[6] nitroso-,[4] nitro-,[4] and azo-compounds.[4] The intermediacy of münchnones is demonstrated by the nature of the products formed when *N*-substituted α-acylaminoacids are treated with acetic anhydride in the presence of dipolarophiles;[2,5,6] the isolated compounds arise from secondary reactions of the initial cycloadducts. Even simple Δ^2-oxazolin-5-ones (saturated azlactones) (3) can react in the mesoionic tautomeric form (4) as shown by the formation of pyrroles when such compounds are heated with acetylenes.[7] Furthermore, the existence of the equilibrium (3) ⇌ (4) has been established spectroscopically in the case of the 2-*p*-nitrophenyl-4-phenyl [8] and 2,4-diphenyl derivatives.[9] Only oxazolium-5-oxides with aryl substituents in both the 2- and 4-positions have been isolated so far, the simplest being the methyldiphenyl compound (1a).[10] Attempts to prepare compounds lacking a substituent at C-4 invariably resulted in the formation of 4-acyl-substituted oxazolium-oxides. Thus, heating 1,2-dihydro-2-oxopyridine-*N*-acetic acid with acetic anhydride gave the *C*-acetyl derivative (5b) rather than the parent münchnone (5a),[11] the action of trifluoroacetic anhydride on *N*-benzoyl-*N*-phenylglycine led to the ketone (1b),[12] treatment of *N*-benzoylsarcosine with dicyclohexylcarbodiimide yielded the acyl derivative (8a),[13] and reaction of *N*-acetyl-*N*-benzylglycine with oxalyl chloride afforded the mesoionic acid chloride (1c).[14] Hence it appears that münchnones unsubstituted in position 4 are so readily attacked by acylating agents that their synthesis requires the absence of such reagents. Deprotonation of the 2,3-disubstituted oxo-oxazolinium salts (6), which are described in the preceding paper,[15] in an indifferent medium offered a means of obtaining the corresponding oxazolium-oxides (7), and we accordingly attempted to prepare such compounds and to study their properties. The chemistry of the bicyclic münchnone (5a), generated from its hydroperchlorate, has already been reported.[16]

Addition of triethylamine to a suspension of 3-methyl-5-oxo-2-phenyl-Δ^2-oxazolinium perchlorate (6a) in dichloromethane gave a yellow solution which almost instantly deposited the dimeric acyloxazolone (8a) in 83% yield. When, however, the salt was slowly added to triethylamine in the same solvent the resulting solution remained clear for several minutes before the dimer began to separate. We suggest that in the first case the oxazolium-oxide (7a), as soon as it is formed, reacts with the cation (6a) to give the product (see Scheme 1); but that in the second, inverse addition experiment the salt is completely deprotonated so that the slower dimerisation involves electrophilic attack by the free münchnone which is a less powerful acylating agent than the cation (Scheme 2). The existence of the mesoionic oxazolone in the solution obtained by the second method was demonstrated by the evolution of carbon dioxide and formation of the pyrrole (9a) when dimethyl acetylenedicarboxylate was added. This reaction proceeds by retro-cycloaddition of the initial adduct (10).[2] The pyrrole was produced in a higher yield by an *in situ* reaction in which triethylamine was added to a mixture of the acetylenic ester and the oxazolinium salt. The unstable münchnone could also be trapped as its trifluoroacetyl derivative (11a), which was obtained when the solution was treated with trifluoroacetic anhydride. Addition of *p*-nitro-, *p*-methoxy-, or *p*-chloro-benzoyl chloride to the solution similarly gave the stable mesoionic ketones (11b—d), respectively. Use of the *in situ* technique again resulted in a higher yield of the

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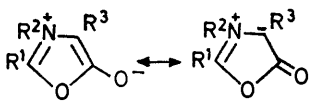
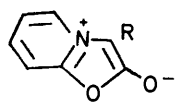


(1) (2) (3) (4)

	R^1	R^2	R^3
a;	Ph	Me	Ph
b;	Ph	Ph	$CO{\cdot}CF_3$
c;	Me	$PhCH_2$	COCl



(5)

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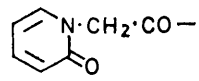
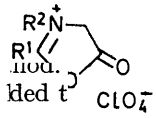
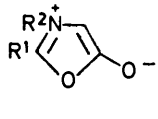
b; R = Ac
c; R = 



(6)



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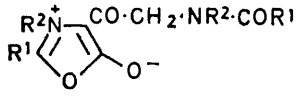

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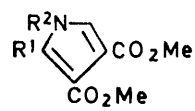
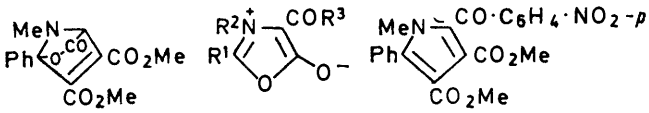


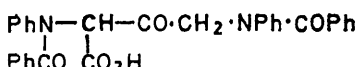
(9)

a; R^1 = Ph, R^2 = Me
b; R^1 = R^2 = Ph
c; R^1 = Me, R^2 = Ph
d; R^1 = p-$O_2N{\cdot}C_6H_4$, R^2 = Ph
e; R^1 = p-$MeO{\cdot}C_6H_4$, R^2 = Ph
f; R^1 = p-ClC_6H_4, R^2 = Me
g; R^1 = p-$O_2N{\cdot}C_6H_4$, R^2 = Me
h; R^1 = Ph_2N, R^2 = Me



(10) (11) (12)

	R^1	R^2	R^3
a;	Ph	Me	CF_3
b;	Ph	Me	p-$O_2N{\cdot}C_6H_4$
c;	Ph	Me	p-$MeO{\cdot}C_6H_4$
d;	Ph	Me	p-ClC_6H_4
e;	p-ClC_6H_4	Me	p-$O_2N{\cdot}C_6H_4$
f;	p-$O_2N{\cdot}C_6H_4$	Me	p-$O_2N{\cdot}C_6H_4$



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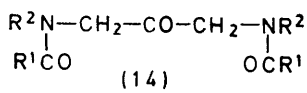
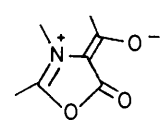
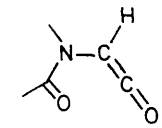


(14)

a; R^1 = R^2 = Ph
b; R^1 = p-$O_2N{\cdot}C_6H_4$, R^2 = Ph
c; R^1 = p-$MeO{\cdot}C_6H_4$, R^2 = Ph
d; R^1 = p-ClC_6H_4, R^2 = Me
e; R^1 = Ph_2N, R^2 = Me



(15)



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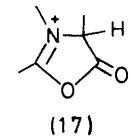

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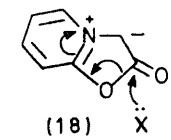
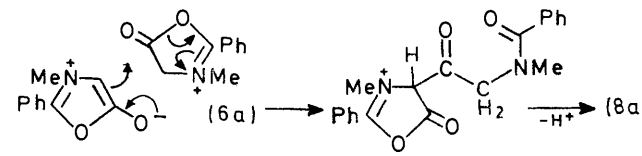


(18) X

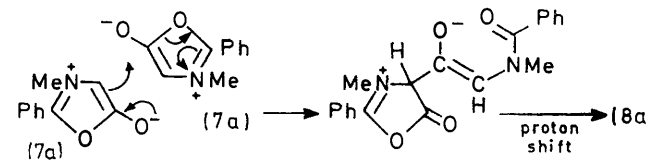
p-nitrobenzoyl derivative. This compound reacted with dimethyl acetylenedicarboxylate under forcing conditions (boiling benzonitrile) to yield the ketonic pyrrole ester (12).

From the diphenyloxazolinium perchlorate (6b) a solution of the mesoionic oxazolone (7b) was prepared;



(7a) (6a) (8a)

SCHEME 1



(7a) (7a) (8a)

SCHEME 2

its decomposition product was, however, not the expected dimeric acyl derivative (8b) but the open-chain ketone (14a). The structure of this compound follows from analysis, the i.r. spectrum, which contained amide and ketone carbonyl bands, and the n.m.r. spectrum, which exhibited aromatic proton signals and a methylene singlet (intensity ratio 5 : 1). We suggest that the dimer (8b) is formed initially and decomposes to the ketone during the work up by hydrolytic ring opening and subsequent decarboxylation of the resulting β-keto-acid (13). The münchnone (7b) was trapped as the pyrrole (9b) and as the trifluoroacetyl derivative (1b) when the parent salt was deprotonated in the presence of dimethyl acetylenedicarboxylate or trifluoroacetic anhydride, respectively.

Treatment of a mixture of the perchlorate (6c) and the acetylenic ester with triethylamine gave the pyrrole (9c); the pyrrole esters (9d—g) were similarly obtained from the salts (6d—g), respectively. The mesoionic oxazolone (7f) was trapped as the stable 4-*p*-nitrobenzoyl derivative (11e); the analogue (11f) was obtained by the *in situ* method. Deprotonation of the oxazolinium salts (6d—f) yielded the acyclic ketones (14b—d), respectively.

We failed to obtain any evidence for the formation of

the 2-diphenylamino-substituted oxazolium-oxide (7h) when deprotonation of its hydroperchlorate was attempted under the usual conditions. The action of triethylamine on the salt (6h) resulted in an intractable mixture, the i.r. spectrum of which did not contain any bands attributable to the oxide (7h), or its expected decomposition products, the dimer (8h) or the symmetrical ketone (14e). It was mentioned in the preceding paper that the perchlorate (6h) could not be condensed with aromatic aldehydes, a reaction which we regard as diagnostic for the intermediacy of mesoionic oxazolones. However, heating a mixture of *N*-(diphenylcarbamoyl)sarcosine, dimethyl acetylenedicarboxylate, and acetic anhydride yielded the diphenylaminopyrrole (9h), demonstrating that the mesoionic compound can be produced under appropriate conditions. Our failure to deprotonate the salt (6h) may be attributed to stabilisation of the cation by conjugation with the 2-diphenylamino-substituent.

The i.r. spectra of the freshly prepared dichloromethane solutions of the unstable mesoionic oxazolones (7) and (5a) [16] exhibited two strong absorptions, at 1730—1740 and 1695—1708 cm^{-1} (see Table 1); compound (7c) decomposed so quickly that its spectrum could not be recorded. Since these bands gradually decreased in intensity they are assigned to the free münchnones.* The stable münchnone (1a) and analogous 2,4-diaryl-3-methyloxazolium-oxides absorb at 1710 cm^{-1} in dichloromethane solution.[10] These values may be compared with the carbonyl stretching frequencies of saturated oxazolin-5-ones (*ca.* 1820 cm^{-1}) and those of their 4-arylidene derivatives (*ca.* 1790 cm^{-1}). The shift to lower frequencies observed in the spectra of the mesoionic compounds can be attributed to the polarity of the exocyclic carbon–oxygen bond, *i.e.* to the aromatic oxide character [*cf.* (1)] of the system. Moreover, the high integrated intensities [10] of the carbonyl bands in the spectra of münchnones are indicative [17a] of a reduced carbonyl bond-order. Arguments based on absorption intensities have also been advanced to support the oxide character of sydnones [17a] and mesoionic 1,3,4-oxadiazolones,[18] whose carbonyl bands lie in the lactone region. The i.r. spectra (Nujol) of the stable acyloxazolium-oxides (11b—f) exhibit cyclic carbonyl absorption at higher frequencies (*ca.* 1760 cm^{-1}) than those of the parent compounds; a further band appears near 1610 cm^{-1}. Similar absorptions were observed in the spectra of acyl derivatives of the bicyclic base (5a).[16] We suggest that the second band is associated with the exocyclic carbonyl group, which must be strongly polarised.† This polarisation, together with the frequency shift of the cyclic carbonyl absorption, indicates greater lactone character [*cf.* (15)] of the acyl derivatives than of the parent molecules. The solution spectra of the dimeric oxazolium-oxides (8a) and (5c) resemble those of compounds (11), exhibiting a band near 1765 (lactone) and two further absorptions in the 1650 and 1630 cm^{-1} regions. One of these must be due to the ketone and the other to the amide carbonyl group, but it is not possible to be more specific.

The spontaneous decomposition of the oxazolium-oxides (5a) and (7) in solution was followed by observing the decay of the i.r. absorption near 1730 cm^{-1}. The disappearance of this band was accompanied by the appearance of two bands near 1760 and 1650 cm^{-1}, which we attribute to the formation of the corresponding dimers (5c) and (8) since the two isolated compounds of this type, the ketones (5c) [16] and (8a), absorb at these frequencies. We failed to obtain any spectroscopic evidence for the intermediacy of acylaminoketens (16), the valency tautomers of mesoionic oxazolium-oxides,[19] in these experiments. The decomposition of the monomeric münchnones was found to follow second-order kinetics. The oxazolinium perchlorate (6a) was deprotonated by amounts of triethylamine varying from 1 to 8 mol. equiv. but the rate of decomposition of the resulting oxazolone (7a) showed no significant variation. The rate constant given for compound (7 g) is considered less precise than the others because, as the parent perchlorate was not crystalline, the initial concentration of the base could not be accurately assessed.

The results of the kinetic experiments are summarised in Table 2. The eight mesoionic oxazolones studied comprise the bicyclic base (5a), four *N*-phenyl compounds (7b—e), and three possessing *N*-methyl substituents (7a, f, and g). The relative rates of dimerisation refer to the comparatively stable pyridine, derivative which, in decimolar solution, has a half-life of 30 min at room temperature. The relative rates show that the mesoionic system is stabilised by the presence of an electron-releasing group (methyl) on the nitrogen atom; the *N*-methyl compounds decompose *ca.* 10 times more slowly than the *N*-phenyl analogues. Aryl substitution at C-2 also inhibits dimerisation; the 2-methyl derivative (7c) decomposed immeasurably fast. Substituents in the aryl groups have little effect; we do not attach any significance to the slight differences in rates of individual members of the 2-aryl-*N*-methyl and 2-aryl-*N*-phenyl series.

Since mesoionic oxazolium-oxides lacking substituents at C-4 decompose by dimerisation, a discussion of their stability must be based on this reaction. It was suggested that this occurs by a substitution process in which one molecule acts as a nucleophile and the other as an

* Splitting of the high-frequency band is also observed in the spectra of some sydnones.[17]

† The doublet at 1802 and 1779 cm^{-1} in the spectrum of the trifluoroacetyl compound (1b) is similarly assigned to the cyclic carbonyl group and a further band at 1642 cm^{-1} to the ketone function. These assignments differ from those made by Singh and Singh,[12] who attributed the first two bands to the cyclic and exocyclic carbonyl groups, respectively. The i.r. spectrum of compound (11a) also exhibits a doublet in the 1800 cm^{-1} region and a second band at 1630 cm^{-1}.

[17] (*a*) B. E. Zaitsev and Y. N. Sheinker, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, 407; (*b*) Y. G. Borodko and Y. K. Syrkin, *Optika i Spektroskopiya*, 1961, **11**, 482.

[18] A. R. McCarthy, W. D. Ollis, A. N. M. Barnes, L. E. Sutton, and C. Ainsworth, *J. Chem. Soc.* (*B*), 1969, 1185.

[19] R. Huisgen, E. Funke, F. C. Schaefer, and R. Knorr, *Angew. Chem. Internat. Edn.*, 1967, **6**, 367.

electrophile (Scheme 2). The nucleophilic reactivity of the mesoionic compounds is shown by the ease with which they are acylated; they are also highly active electrophiles, being easily attacked at C-5 by amines and not known. It can only be suggested that the nucleophilic activity of the mesoionic oxazolones is not the sole or predominant factor since, if it were, aryl substitution at C-2 and the presence of an electron-donating group

TABLE 1

Characteristic bands in the i.r. spectra of dichloromethane solutions of oxazolium-5-oxides

Oxazolium oxide	(5a)	(7a)	(7b)	(7c)	(7d)	(7e)	(7f)	(7g)
$\nu_{max.}/cm^{-1}$	1740, 1708	1728, 1693	1738, 1695	Not observable	1743, 1700	1730, 1693	1730, 1694	1735, 1694

TABLE 2

Dimerisation of oxazolium-5-oxides in dichloromethane at 25°

Compound	(5a)	(7a)	(7b)	(7c)	(7d)	(7e)	(7f)	(7g)
10^3k_2/l mol^{-1} s^{-1}	5·5 ± 0·3	8·4 ± 0·4	74 ± 4		59 ± 3	87 ± 4	13 ± 1	(11·5) *
Relative rate	1	1·5	13·5	High	11	16	2·4	*ca.* 2·1

* Approximate.

TABLE 3

1,3-Di(acylamino)propan-2-ones (14)

Oxazolinium perchlorate	Product	Yield (%)	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}/cm^{-1}$	τ
(6b)	(14a)	97	187 [a]	77·8	5·45	6·4	$C_{29}H_{24}N_2O_3$	77·7	5·4	6·25	1749, 1648	2·55—2·95 (m, 2 × CPh), 2·88 (s, 2 × NPh), 5·21 (s, 2 × CH_2)
(6d)	(14b)	94	211—212 [a]	64·3	4·2	10·5	$C_{29}H_{22}N_4O_7$	64·7	4·1	10·4	1744, 1645	1·91—2·59 (m, 2 × CAr), 2·83 (s, 2 × NPh), 5·17 (s, 2 × CH_2)
(6e)	(14c)	82·5	139·5 [a]	73·3	5·5	5·5	$C_{31}H_{28}N_2O_5$	73·2	5·55	5·5	1743, 1630	2·63—3·41 (m, 2 × CAr), 2·84 (s, 2 × NPh), 5·20 (s, 2 × CH_2), 6·25 (s, 2 × Me)
(6f)	(14d)	58·8	151 [a]	58·05	4·7	7·2	$C_{19}H_{18}Cl_2N_2O_3$	58·0	4·6	7·1	1732, 1648, 1618	2·59br (2 × Ar), 5·63 (s, 2 × CH_2), 6·91 (s, 2 × Me)

[a] From ethanol.

TABLE 4

N-Substituted dimethyl pyrrole-3,4-dicarboxylates (9)

Pyrrole	Yield (%)	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}/cm^{-1}$
(9a)	73,[a] 80·5 [b]	117—118 [c]								
(9b)	80 [d]	122—122·5 [e]	71·8	5·2	4·35	$C_{20}H_{17}NO_4$	71·6	5·1	4·2	3140w, 1720, 1598
(9c)	78·7 [b]	67—69 [f]								
(9d)	21,[g] 69 [b]	194·5 [h]	63·4	4·3	7·3	$C_{20}H_{16}N_2O_6$	63·15	4·2	7·4	3128w, 1713
(9e)	64·6 [b]	133—133·5 [i]	69·0	5·2	3·8	$C_{21}H_{19}NO_5$	69·0	5·25	3·8	3122w, 1738, 1718
(9f)	85·2 [b]	102·5—103 [h]	58·75	4·5	4·6	$C_{15}H_{14}ClNO_4$	58·55	4·6	4·55	3138m, 1715, 1705
(9g)	52·5 [b]	155 [h]	56·5	4·4	8·75	$C_{15}H_{14}N_2O_6$	56·6	4·4	8·8	3150m, 1699

[a] Method C. [b] Method D. [c] K. T. Potts and D. N. Roy (*Chem. Comm.*, 1968, 1061) give m.p. 117—118°. [d] Prepared in benzene by Method D. [e] From methanol. [f] Lit.,[2] m.p. 69—70°. [g] Method C. The ketone (14b) was also isolated in 26% yield by chromatography. [h] From ethanol. [i] From aqueous ethanol.

TABLE 5

Anhydro-4-acyl-5-hydroxyoxazolium hydroxides (11)

Salt	Product	Yield (%)	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}/cm^{-1}$
(6a)	(11a)	99·6 [a]	161—163° [b]								1803, 1787, 1631 [c]
(6a)	(11b)	77,[d] 86·4 [e]	226 [f,g]	62·65	3·9	8·6	$C_{17}H_{12}N_2O_5$	62·95	3·7	8·65	1760, 1617, 1608, 1588
(6a)	(11c)	38 [d]	163—164 [h]	69·95	5·0	4·6	$C_{18}H_{15}NO_4$	69·9	4·9	4·5	1760, 1608, 1590, 1565
(6a)	(11d)	51 [d]	184—184·5 [i]	64·6	4·1	4·7	$C_{17}H_{12}ClNO_3$	65·1	3·9	4·45	1750, 1608, 1588, 1562
(6b)	(1b)	60,[e] 91 [j]	189—191 [k]								1798, 1780, 1642 [c]
(6f)	(11e)	58·5 [d]	223—225·5 [f,g,l]	57·4	3·1	7·4	$C_{17}H_{11}ClN_2O_5$	56·9	3·1	7·8	1753, 1612, 1587
(6g)	(11f)	60 [e]	250—251 [f,g]	55·3	2·9	11·2	$C_{17}H_{11}N_3O_7$	55·3	3·0	11·4	1759, 1614, 1588

[a] Method E, 0·005 mol scale. [b] Ref. 13 gives m.p. 161·5—163°. [c] In chloroform. [d] Method E. [e] Method F. [f] With decomposition. [g] From acetonitrile. [h] Purified by chromatography. [i] From benzene. [j] Method F, 0·003 mol scale. Anhydrous sodium carbonate was used in place of triethylamine. [k] Identified by direct comparison with an authentic specimen.[12] [l] Sensitive to light.

alcohols to give derivatives of α-acylamino-acids.[10] It is difficult to interpret the effect of substituents at C-2 and at the nitrogen atom on the velocity of the complex dimerisation process, since the rate-determining step is on the nitrogen atom should, by stabilising the Wheland intermediate (17), enhance the rate, contrary to what is observed. The electrophilic reactivity of the compounds must also be taken into account; the dimerisation is

certainly very fast when the oxazolinium cation, a powerful electrophile, is involved (see Scheme 1). The relative stability of the bicyclic oxazolium-oxide (5a) may possibly be due to its comparatively low reactivity towards nucleophiles: the ring-opening process (18) results in the destruction of the aromatic pyridinium structure.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra refer to Nujol mulls unless stated otherwise. N.m.r. spectra were determined at 60 MHz for deuteriochloroform solutions on a Perkin-Elmer R10 spectrometer.

Deprotonation of 5-Oxo-Δ^2-oxazolinium Salts.—Method A. Triethylamine (3·3 ml) was added slowly to a stirred suspension of the perchlorate (6a) (0·01 mol) in dichloromethane (10 ml) at −15°; the resulting yellow solution deposited the dimeric oxazolone (8a) (1·6 g, 83%) within a few seconds; m.p. 175—177° (lit.,[13] 175—176°), identified by direct comparison with a specimen prepared according to the published [13] procedure, $\nu_{max.}$ (Nujol) 1740, 1630sh, and 1620 cm^{-1}; $\nu_{max.}$ ($CHCl_3$) 1762, 1650, and 1630 cm^{-1}.

Method B. Addition of the perchlorate (0·01 mol) in small portions to a stirred solution of triethylamine (3·3 ml) in dichloromethane (15 ml) at −15° gave a yellow solution which remained clear for several minutes before crystals appeared. The mixture was kept at room temperature overnight and then cooled to −15°; the precipitated dimer (1·6 g) was identified by m.p., mixed m.p., and i.r. spectrum.

Deprotonation of the oxazolinium salts (6b, d, e, and f) by method A gave solutions which were evaporated. The oily residues solidified in contact with cold 50% aqueous ethanol (20 ml) to give the *ketones* listed in Table 3.

Formation of Pyrroles from Oxazolium-5-oxides (Table 4).—Method C. The solution of the mesoionic compound prepared by method B was at once treated with dimethyl acetylenedicarboxylate (1·3 g). There was a vigorous effervescence. The solvent was removed; the oily residue was suspended in water and the mixture was extracted with chloroform (3 × 20 ml). The combined extracts were dried ($MgSO_4$), concentrated, and chromatographed on neutral alumina. The product was eluted with benzene–chloroform mixtures of increasing polarity.

Method D. The oxazolinium perchlorate (0·01 mol) was added to an ice-cold solution of the acetylenic ester (1·3 g) in acetonitrile (15 ml); the mixture was stirred and triethylamine (1·4 g) was slowly added. Stirring was continued for 20 min and the solution was then poured into water and the product isolated as just described.

4-Acyloxazolium-5-oxides (11) (Table 5).—Method E. A solution of a mesoionic oxazolone prepared by method B was treated with an arenecarbonyl chloride (0·01 mol) or trifluoroacetic anhydride (4·0 g). The acyl derivative usually crystallised on cooling; if it did not the solvent was removed, the residue was extracted with boiling benzene (2 × 10 ml), and the product was isolated by chromatography on alumina and elution with benzene–chloroform.

Method F. Triethylamine (3·3 ml) was added to a stirred mixture of an oxazolinium perchlorate (0·01 mol), an arenecarbonyl chloride (0·01 mol) [or trifluoroacetic anhydride (4·0 g)], and acetonitrile (15 ml). The mixture was kept at 0° overnight and the product was collected.

Dimethyl 1-Methyl-2-p-nitrobenzoylpyrrole-3,4-dicarboxylate (12).—A solution of the *p*-nitrobenzoyloxazolium oxide (11b) (1·62 g) and dimethyl acetylenedicarboxylate (0·6 g) in benzonitrile (10 ml) was boiled under reflux for 40 min. The solvent was removed *in vacuo*; the residue solidified in contact with ethanol (10 ml) to give the *pyrrole* (1·95 g, 93%), m.p. 161—162° (from ethanol), $\nu_{max.}$ 1718br and 1637 cm^{-1}, τ 1·62—2·15 (m, Ar), 2·55 (s, Ph), 6·37 (s, Me), 6·40 (s, Me), and 6·68 (s, Me) (Found: C, 63·0; H, 4·4; N, 6·55. $C_{22}H_{18}N_2O_7$ requires C, 62·6; H, 4·3; N, 6·6%).

Attempts to generate Anhydro-5-hydroxy-3-methyl-2-diphenylamino-oxazolium Hydroxide (7h).—A stirred suspension of the diphenylamino-oxazolinium perchlorate (6h) (1·83 g) in dichloromethane (15 ml) was treated with triethylamine (15 ml). The pale brown solution was evaporated under reduced pressure after 30 min, 50% aqueous ethanol (30 ml) was added to the residual oil, and the mixture was kept at 0° overnight. The resulting semi-solid was shown by t.l.c. to be composed of at least six components; its i.r. spectrum showed the presence of perchlorate ion and absence of absorption in the 1700—1800 cm^{-1} range.

A solution of *N*-(diphenylcarbamoyl)sarcosine (5·68 g) and dimethyl acetylenedicarboxylate (2·5 ml) in acetic anhydride (30 ml) was boiled under reflux for 30 min. The pale brown solution was poured into saturated aqueous sodium carbonate (400 ml) and the mixture was extracted with chloroform (3 × 50 ml). The combined extracts were dried ($MgSO_4$) and evaporated. The residue solidified in contact with ethanol (10 ml) to yield *dimethyl 1-methyl-2-(diphenylamino)pyrrole-3,4-dicarboxylate* (9h) (2·9 g, 39·8%), m.p. 125° (from ethanol), $\nu_{max.}$ 3130w, 1735, and 1715 cm^{-1} (Found: C, 69·15; H, 5·55; N, 7·6. $C_{21}H_{20}N_2O_4$ requires C, 69·2; H, 5·5; N, 7·7%).

Kinetic Experiments.—Solutions of the mesoionic oxazolium-5-oxides were prepared by adding the appropriate amount of oxazolinium perchlorate to a twofold excess of purified triethylamine in dry dichloromethane (5 ml) at −15°. I.r. spectra of 0·05M- and 0·1M-solutions were recorded by rapidly scanning in the range 1650—1850 cm^{-1} at *ca.* 35 s intervals. The freshly prepared solutions showed two absorptions, at *ca.* 1730 and 1695 cm^{-1}, which decayed during the experiment to be replaced by bands at *ca.* 1760 and 1650 cm^{-1}. The rate of decay of the 1730 cm^{-1} absorptions was in good agreement with second-order kinetics in all cases; values for the rate constant for repeated runs were reproducible within 5%. The mesoionic oxazolone (7a) was studied in several experiments in which the concentration of triethylamine was varied from 1 to 8 mol. equiv. but the rate constant remained essentially the same.

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