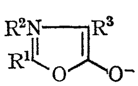
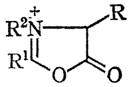
The Chemistry of a Mesoionic Oxazolone

By G. V. BOYD* and P. H. WRIGHT
(*Department of Chemistry, Chelsea College of Science and Technology, London, S.W.3*)

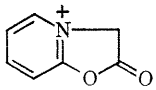
CYCLOADDITION reactions of mesoionic oxazol-5-ones (I) have been investigated[1] but little else has been recorded about their chemistry. These compounds are usually prepared by dehydration of α-acylamino-acids which, in the absence of dipolarophiles, leads to stabilised ozaxolones having an acyl group at C-4,[2-4] a notable exception being the diphenyl-derivative (I; $R^1 = R^3 =$ Ph, $R^2 =$ Me).[1] Simpler members of this class have not been available and consequently no substitution reactions have been described. We have recently found[5] that such compounds can be generated by deprotonation of oxazol-5-onium perchlorates (II; $R^3 =$ H) and we now report on the chemistry of a representative, anhydro-2-hydroxyoxazolo[3,2-*a*]pyridinium hydroxide (IV), obtained from the perchlorate (III).[5]



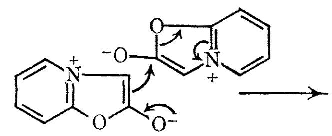
(I)



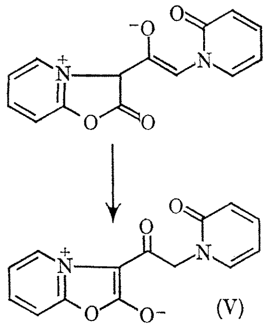
(II) ClO_4^-



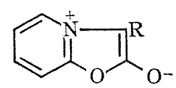
(III) ClO_4^-



(IV)



(V)



(VI)

When this salt is added in small portions to a stirred solution of an excess of triethylamine in dichloromethane a clear straw-coloured solution [λ_{max} 320 infl., 361 nm.] results which slowly deposits a colourless solid, m.p. 282° (decomp.), [λ_{max} (CH_2Cl_2) 241, 257, and 340 nm.]. Analytical,† and mass spectral (*m/e* 270, M^+) data show this to be the dimer (V). This is supported by the n.m.r. spectrum in trifluoroacetic acid solution in which the compound is protonated on carbon [τ 1·47—1·92 (4H, m), 2·24—2·63 (4H, m), 4·03 (CH, s), 4·37 (CH_2, s)] and the i.r. spectrum which exhibits the characteristic high-frequency oxazolone absorption at 1766 cm.$^{-1}$ (Table) and a band at 1653 cm.$^{-1}$ (pyridone CO). The assignment of two further bands at 1574 and 1630 cm.$^{-1}$, one of which is due to the ketone CO, is under current investigation.

We suggest that the dimer is formed from the oxazolone (IV) by the mechanism shown in which one molecule functions as an electrophile and the other as a nucleophile. The

---

† Satisfactory analyses have been obtained for all new compounds whose melting points are given.

dimer is formed almost instantly in quantitative yield by the inverse addition of triethylamine to a suspension of the salt (III) in dichloromethane; we propose that here the oxazolone reacts with the strongly electrophilic cation. The dimer is also obtained (90%) by the action[4] of dicyclohexylcarbodi-imide on 1-carboxymethyl-2-pyridone.

Substituted anhydro-2-hydroxyoxazolo[3,2-a]*pyridinium hydroxides* (*VI*)

Comp.	R	Yield (%)	M.p.	I.r. (Nujol) (cm.$^{-1}$)
(a)	Bz	83	200[a]	1787
(b)	*p*-$NO_2 \cdot C_6H_4 \cdot CO$	74	300[a]	1768
(c)	$CF_3 \cdot CO$	91	164	1802
(d)	Ac	79	170[b]	1755
(e)	*p*-$NO_2 \cdot C_6H_4 \cdot N_2$	60	236	1806

[a] With decomposition; [b] lit. (ref. 2), 170°.

All attempts to isolate the mesoionic oxazolone (IV) resulted in formation of the dimer, but we were able to carry out substitution reactions on the monomer in solution. Thus, benzoyl chloride, *p*-nitrobenzoyl chloride, and trifluoracetic anhydride afforded the stable derivatives (VI a—c), respectively (Table). Similarly, acetyl chloride gave the known compound (VId). The oxazolopyridine coupled with *p*-nitrobenzenediazonium fluoroborate to yield the stable deep-red azo-compound (VIe).

The oxazolone (IV) is susceptible to attack by nucleophilic reagents with ring-fission; for example, addition of aniline to the freshly prepared solution gives (98%) the anilide of 1-carboxymethyl-2-pyridone, m.p. 280·5°, i.r. 1657, 1688 cm.$^{-1}$

We thank the Governors of this College for a Research Studentship (to P. H. W.).

(*Received, December* 9*th*, 1968; *Com.* 1688.)

[1] R. Huisgen, *Chem. Soc. Special Publ. No.* 21, 1967, p. 51; R. Huisgen, R. Gotthardt, H. O. Baeyer, and F. C. Schaefer, *Angew. Chem.*, 1964, **76**, 185; R. Huisgen and E. Funke, *ibid.*, 1967, **79**, 320.

[2] A. Lawson and D. H. Miles, *J. Chem. Soc.*, 1959, 2865.

[3] G. Singh and S. Singh, *Tetrahedron Letters*, 1964, 3789.

[4] C. V. Greco, R. P. Gray, and V. G. Grosso, *J. Org. Chem.*, 1967, **32**, 4101.

[5] G. V. Boyd, *Chem. Comm.*, 1968, 1410.