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THE FORMATION OF 4-IMIDAZOLIDINONES FROM 2-PHENYLOXAZOLONIUM PERCHLORATE AND SCHIFF BASES

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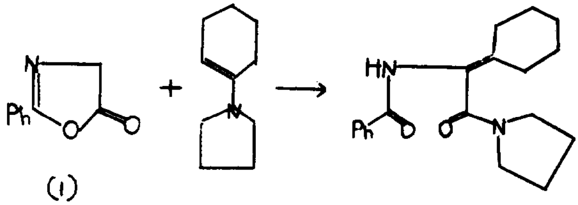
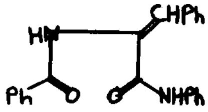
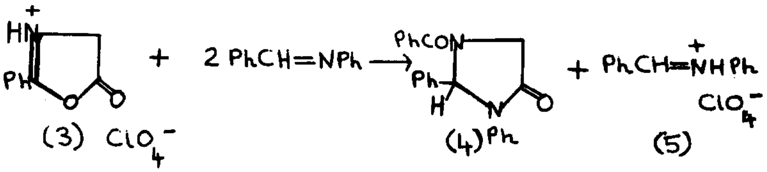
We have recently reported[1] that 5-oxazolones react with enamines to yield α-acylamino-acrylamides, e.g.

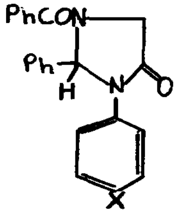

(1)


(2)

It has now been found that analogous products are obtained from oxazolones and Schiff bases; thus α-benzamidocinnamanilide (2) is formed when the azlactone (1) is treated with benzylideneaniline. Replacement of the oxazolone by its hydroperchlorate (3)[2] radically alters the course of the reaction: addition of two equivalents of benzylideneaniline to a suspension of the perchlorate in cold dioxan rapidly yields the known[3] 1-benzoyl-2,3-diphenylimidazolin-4-one (4) (54%), together with the theoretical amount of benzylideneanilinium perchlorate (5).


(3) (4) (5)

The imidazolidinones (6 a - c) were obtained in yields of 16 - 34% by reaction of the perchlorate (3) with appropriate Schiff bases; similarly, dicyclohexylcarbodi-imide gave **compound (7) (29%). The products exhibit** carbonyl absorption at 1700 cm.$^{-1}$; satisfactory **analytical data were** obtained for these new compounds.

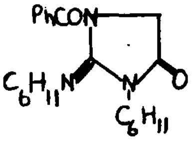


(6)

a; X = Cl, m.p. 228 - 230°

b; X = OMe, m.p. 235 - 237°

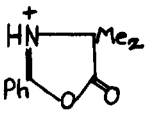
c; X = NO_2, m.p. 210 - 212°



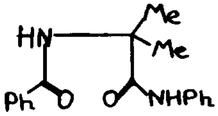
(7)

m.p. 188 - 190°

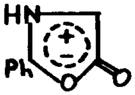
The mechanism of imidazolidinone formation is not yet clear; however, the following **points are relevant.** Initial proton transfer from the perchlorate (3) to the Schiff base **to form the oxazolone (1) is ruled out by our observation** that this compound reacts with **benzylideneaniline to yield the amide (2),** and with benzylideneanilinium perchlorate to **give hippuranilide. Attack by the Schiff base on the carbonyl group** in the cation of (3) **and subsequent cyclisation** is considered improbable because 4,4-dimethyl-2-phenyl-5-**oxazolonium perchlorate (8) does not yield an** imidazolidinone on treatment with benzylidene**aniline; the anilide (9) is formed instead. The** reactions of the oxazolonium salt (3) **therefore probably proceed by initial proton** abstraction from carbon to yield the mesoionic **tautomer (10) of the azlactone (1).** *Such species have been detected* spectroscopically[4,5] **in solutions of oxazolones and their intermediacy** is involved in cycloaddition reactions of **these compounds.[5] Moreover, the N-substituted mesoionic** oxazolone (11) reacts with Schiff **bases to yield azetidinones;[6] this reaction is** believed to proceed by valency isomerisation **to the keten (12), followed by** cycloaddition.[6] In the present case an analogous sequence **would lead to the azetidinone (13) which is known[3]** to rearrange to the imidazolidinone (4). **However, this pathway appears unlikely to us** because the rearrangment (13) ⟶ (4) occurs **only at elevated temperatures and we failed** to find any evidence (νCO, 1750 - 1800 cm.$^{-1}$) *for the* **intermediary** *of the azetidinone when the reaction between the oxazolonium perchlorate* **and the benzylideneaniline** was followed by infra-red spectroscopy.



(8) ClO_4^-

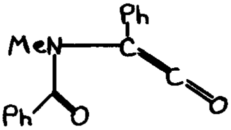


(9)

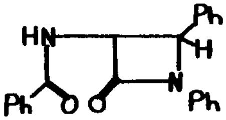


(10)

(11)

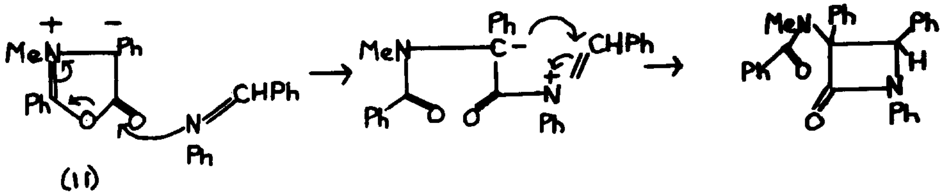


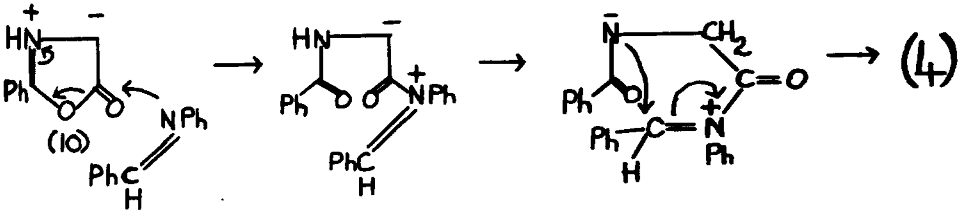
(12)



(13)

It is possible that formation of azetidinones from the N-substituted mesoionic oxazolone (11) and of imidazolidinones from the mesoionic tautomer (10) both proceed by initial attack of the imine on the carbonyl group; this is followed by carbon-carbon bond formation in the former reaction, while in the latter case a prototropic shift intervenes and an imidazolidinone is produced:





Further studies on this and related reactions are in progress.

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