

Reactions of carbonyl compounds in basic solutions. Part 35¹

The alkaline hydrolysis and reactivity – structure – spectra correlations of (*Z*)-4-(substituted benzylidene)-2-phenyl-4*H*-oxazol-5-ones

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The kinetics of the alkaline hydrolysis and the configuration, conformation and electronic structure were studied using IR, NMR spectroscopy, X-ray analysis and AM1 theoretical calculations for a series of (*Z*)-4-(substituted benzylidene)-2-phenyl-4*H*-oxazol-5-ones (**1**) and compared with analogous results reported for (*E*)-4-benzylidene-2-phenyl-4*H*-furan-5-ones (**5**) and related compounds.

Keywords: carbonyl compounds, basic solutions

Alkaline hydrolysis and reactivity–structure–spectra correlations were investigated recently^{2–5} for several series of substituted five–membered ring unsaturated lactones. However, the reactivity of five-membered ring unsaturated azlactones (**1**) in base-catalysed ring fission, as well as their spectral properties, has not received attention.

The results of NMR and IR spectroscopy as well as the single crystal X-ray analysis (for compound **1l**) and the results of AM1 theoretical calculations showed that azlactones (**1a** – **1n**) have the *Z*-configuration and the conformation with the substituent X pointing towards the vinyl group hydrogen atom (in the case of 2- and 3- substituted derivatives) (see Fig. 1 for compound **1l**). The patterns of the absorption bands of the IR C=O stretching vibrations of compounds **1** are similar to those of isobenzofuranones,^{4,5,10} which exhibit a splitting caused by Fermi resonance. Therefore, for further reactivity – structure – spectra correlation analysis the unperturbed $\nu(\text{C}=\text{O})$ wave numbers were calculated by the Langseth – Lord – Nyquist method.¹¹ In ¹H, ¹³C and ¹⁵N NMR spectra the signals relevant to the structure were completely assigned. Further, the AM1 bond orders and Mulliken charges were calculated for the series of azlactones **1**.

The rate coefficients for the alkaline hydrolysis of the series of compounds **1** in 70% (v/v) aqueous dioxane were measured at various temperatures and the activation parameters were determined. The reaction was found to be first order both in substrate and hydroxide anion. Preparative alkaline hydrolysis of the parent compound **1d**, followed by isolation and identification, confirmed that the reaction products are the 2-benzamido-3-arylpropenoic acids. The reaction pathway is shown in Scheme 2 whereby the rate determining step is con-

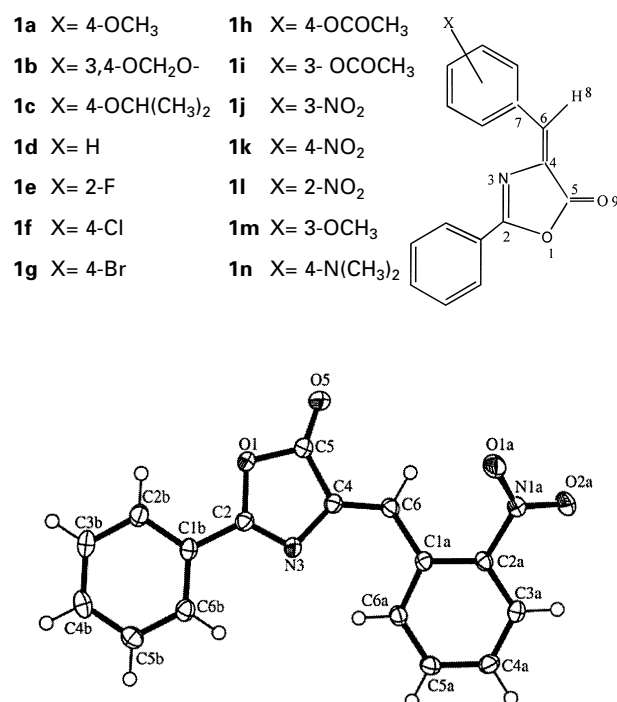
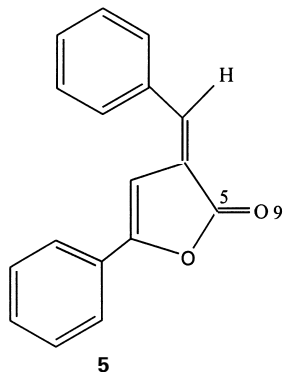


Fig. 1 ORTEP-III plot of 4-(2-nitrobenzylidene)-2-phenyl-4*H*-oxazol-5-one (**1l**) showing the right configuration and preferred conformation (**aa**) of compound.

sidered to be k_1' . The rate constants for the azlactones (**1**) are about 13 times larger than for analogous (*E*)-4-benzylidene-2-phenyl-4*H*-furan-5-ones (**5**).² The IR and theoretical data show that the polarity of the C=O bond decreases by

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introduction of a nitrogen atom into position 3 of the lactone ring. This can be explained as a cross conjugation of the nitrogen and the ring oxygen atoms in the ground state of **1**. The azlactones **1** are essentially cyclic imino-anhydrides and would be expected to be more reactive than the simple lactones **5**. As expected therefore, the comparison of the ρ values for $\log k_2$ vs substituent constant correlations shows that the azlactone system (**1**) is somewhat less sensitive to the substituent effects than the furanone system (**5**).²



The kinetic values, wave numbers of IR stretching vibrations, NMR chemical shifts and the AM1 theoretical data were mutually correlated, as well as being correlated with substituent constants. The results of these correlations shown good agreement between the reactivity of the azlactone system in the base-catalysed ring fission and the electronic structure in the ground state of the above system.

Techniques used: IR spectroscopy, ¹H, ¹³C, ¹⁵N NMR, UV-VIS spectroscopy (monitoring of the kinetic behaviour), X-ray diffraction analysis.

References: 36

Schemes: 2

Fig. 1: ORTEP-III plot of 4-(2-nitrobenzylidene)-2-phenyl-4H-oxazol-5-one (**11**) showing the right configuration and preferential conformation (**aa**) of compound

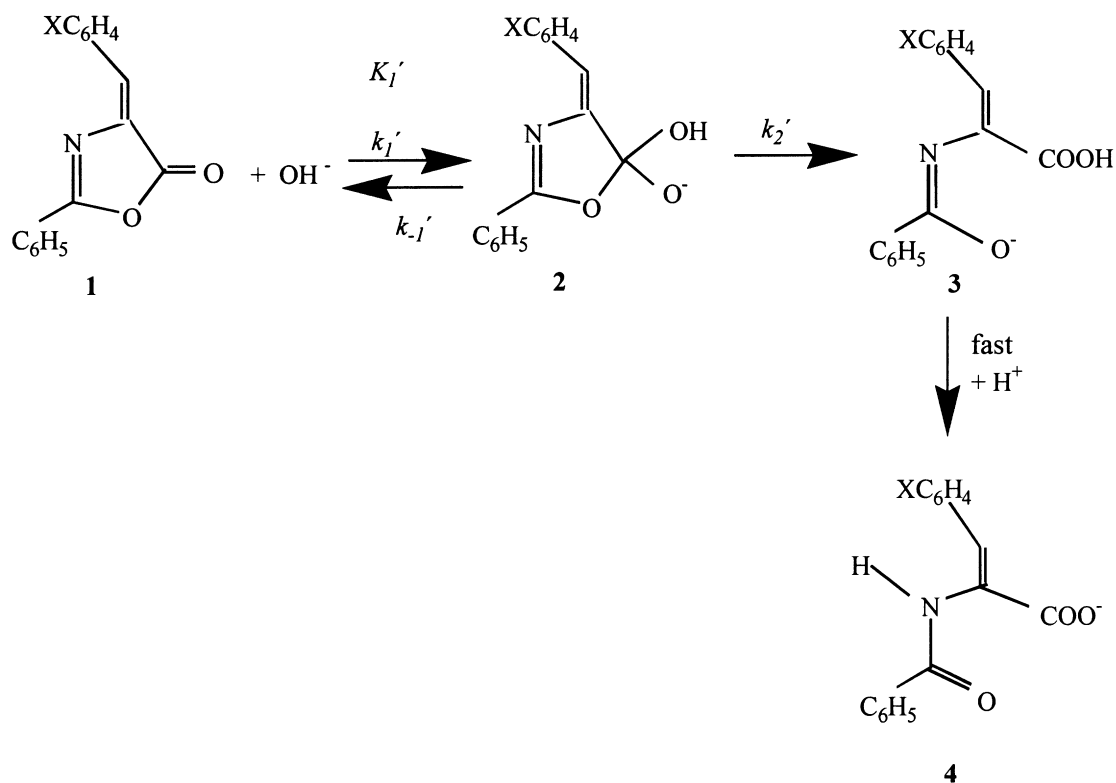
Fig. 2: Dependence of the rate coefficients of alkaline hydrolysis on σ^+ values for (Z)-4-(substituted benzylidene)-2-phenyl-4H-oxazol-5-ones(**1**)

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Scheme 2