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Reactions of Carbonyl Compounds in Basic Solutions. Part 29.[1] The Alkaline Hydrolysis of Unsaturated Lactones

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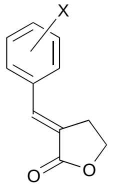
The kinetics of the alkaline hydrolysis of a series of unsaturated lactones (furanones, pyranones and pyrones) and esters (propenoates) have been investigated and the effects of substitution, relative rates and activation parameters are discussed in relation to detailed mechanisms and structure–reactivity.

Relatively small ring lactones are constrained to form their ester group in a *cis*/*E* conformation and are markedly more reactive than acyclic esters or relatively large ring lactones, which are present in *trans*/*Z* form.[2–4] The reactivity of unsaturated small-ring lactones has not received as much attention, except for the alkaline hydrolysis of coumarins[5] and of ring (pseudo) esters of unsaturated or aromatic keto or formyl carboxylic acids.[6,7] In the present study, the kinetics of alkaline hydrolysis of a series of substituted (*E*)-3-phenylmethylidene-4,5-dihydrofuran-2(3*H*)-ones (**1**), (*E*)-3-phenylmethylidene-3,4,5,6-tetrahydropyran-2-ones (**2**), (*E*)-5-phenyl-3-phenylmethylidenefuran-2(3*H*)-ones (**3**), (*Z*)-3-phenylmethylideneisobenzofuran-1(3*H*)-ones (**4**), 4,6-diphenyl-2-pyrone (**5**) and ethyl (*E*)-3-phenylprop-2-enoates (cinnamates) (**6**) to give the corresponding carboxylic acids have been investigated in 70% (v/v) 1,4-dioxane–water. The reactions are all first-order both in substrate and hydroxide anion. The relative rates at 30.0 °C of the lactones **1**, **2**, **3**, **4** and **5** to open-chain model systems are *ca.* 28, 180, 20, 2.2 and 0.23, respectively. There does appear, in general, to be a *reduced* increase in reactivity of the unsaturated lactones, compared to the saturated systems. The rate-determining step has been considered to be the formation of the tetrahedral intermediate. The Hammett equation has been used to assess the effect of substitution on reactivity in the systems , **2**, **3** (5-phenyl), **3** (3-phenylmethylidene), **4** and **6** to give ρ values of *ca.* 1.16, 1.28, 0.94, 1.13, 1.54 and 0.65, respectively. The enhanced reactivity of the unsaturated lactones, compared to open-chain esters, where such exists, appears more likely to arise from an electrostatic source, modified here by resonance interactions. A further significant factor would appear to be the conformations of the unsaturated five- and six-membered rings, compared to the saturated rings in the simple lactones originally studied.[2,3]



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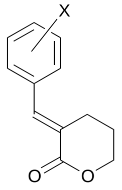

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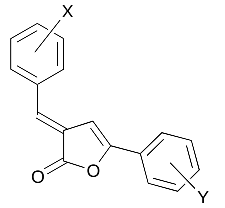

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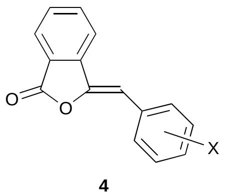

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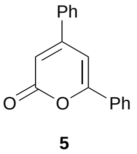

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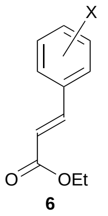

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Techniques used: UV–VIS, ^{1}H and ^{13}C NMR

References: 36

Schemes: 1

Table 1: Rate coefficients (k_2) for the alkaline hydrolysis of the unsaturated lactones **1**, **2**, **3**, **4** and **5** and esters **6** in 70% (v/v) aqueous 1,4-dioxane at 30.0 °C

Table 2: Activation parameters for the alkaline hydrolysis of the parent unsaturated lactones **1**, **2**, **3**, **4** and **5** and ester **6** in 70% (v/v) 1,4-dioxane–water at 30 °C, together with their solvent ratio and carbonyl stretching frequency in carbon tetrachloride

Table 3: Hammett reaction constants (ρ) for the alkaline hydrolysis of the unsaturated lactones **1**, **2**, **3** and **4** and ester **6** in 70% (v/v) aqueous 1,4-dioxane at 30 °C

Table 4: Physical constants of previously unreported unsaturated lactones

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