

TRANSITION METALS CATALYSED REARRANGEMENTS OF β -LACTONES

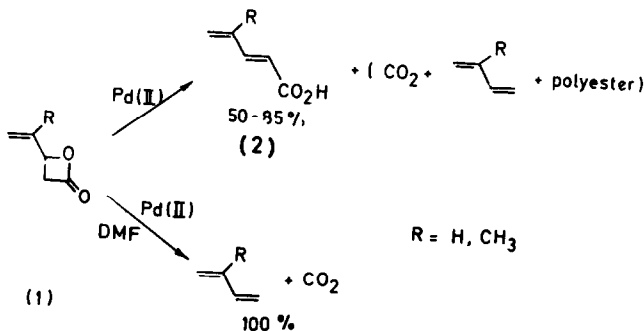
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The ring opening of β -lactones via cleavage of the acyl-oxygen or alkyl-oxygen bond is well documented¹⁾, the tendency to one or other mode depending on the reactions conditions.

On the contrary, the direct rearrangement of β -lactones to α,β -unsaturated acids has not been described. Although the "destructive distillation" of the low molecular weight polyesters²⁾ from the reaction of ketene and aldehydes has led to the formation of such unsaturated acids, in most cases, the β -lactones were shown not to be intermediates in the formation of those polyesters³⁾.

On the other hand, transition metal induced rearrangements of heterocycles are of considerable interest⁴⁾ and we now wish to report the facile isomerization of some β -lactones to unsaturated acids : 3-hydroxy-4-pentenoic acid lactone (1, R = H) rearranges smoothly at room temperature to E-1,3-butadiene-1-carboxylic acid (2, R = H) in the presence of a catalytic amount of a palladium (II) salt.



Best yields in (2) are obtained when the reaction is stopped just after the consumption of the lactone, limiting the subsequent oligomerization of the acid formed.

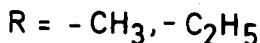
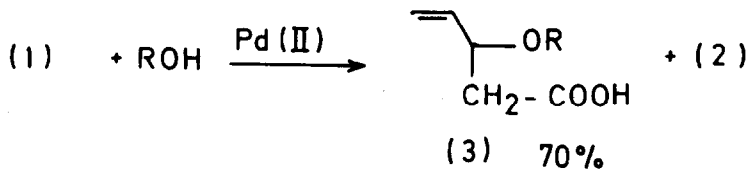
In poorly coordinative solvents or neat, yields up to 85 % in unsaturated acids are obtained.

Besides the evolution of a little CO_2 and the formation of the corresponding diolefin, some polymeric materials, identified as polyester by IR are also formed during the reaction.

On the contrary, in solvents such as CH_3CN or DMF, a fast and quantitative evolution of CO_2 and butadiene takes place at room temperature.

Some other transition metals derivatives (Rh(I), Ag(I), Rh(III) inter alia) also catalyse the reactions but with definitively poorer yields in (2).

Alcoholysis of the lactone using Na_2PdCl_4 in catalytic amount supports indeed the alkyl-oxygen ring opening of the lactone : (3) is isolated in 70 % yield, as characterized by IR and NMR spectra of the $\text{R} = \text{C}_2\text{H}_5$ derivative :



IR - CHCl_3 -

OH, $3500\text{-}2500\text{ cm}^{-1}$; C = O, 1715; C = C, 1645; C - O - C, 1088.

NMR - CDCl_3 - 100 MHz

- CH_3 (t), $\delta = 1.17$ ppm; - OCH_2 - (m), 3.51, aniso chronous H;

- $\text{CH}_2 - \text{CO}_2$ \ominus (AB), A 2.81, B, 2.67, $J_{\text{AB}} = 15.5$ Hz, $J_{\text{AX}} = 8.35$, $J_{\text{BX}} = 5.2$;

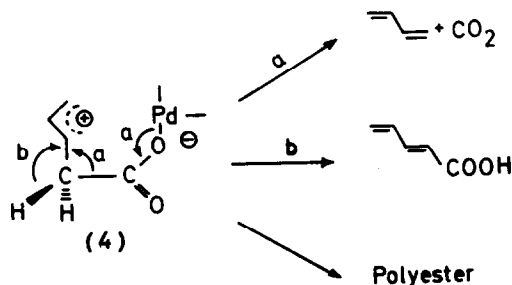
- CH - O - (X, broad quartet), 4.18; $\text{H}_2\text{C} = \text{CH}$ - (ABC), 5.10-5.90,

$J_{\text{CX}} = 7$ Hz; OH (s), 10.28.

Although π -allylic intermediates formed by proton transfer cannot be ruled out at this time, (diketene has been shown to react via such moderately

stable intermediates ^{4b}), the olefinic bond assistance to the ring opening seems obvious ((I), R = CH₃ reacts more slowly than (I), R = H), which is consistent with a highly favoured alkyl-oxygen cleavage. That can be compared to the recently described reaction of a β-thioalkyl-β-lactone in which a sulfur assistance to the opening has been proposed⁵).

A transition state such as (4), possibly with stabilization in the metal coordination sphere of the positive charge generated by the ring opening, is able to explain the formation of the different compounds obtained in the reaction.



Anyhow, the striking ligand effects observed speak in favour of a coordinative type of catalysis.

For example, the addition of trimethylphosphite (TMP) in the ratio TMP/Pd(II) = 4, greatly enhances the rate of the reaction. Under these conditions, there is no longer any CO₂ evolved and the yields in (2) are practically quantitative.

More basic ligands (alkyl and aryl phosphines) favour the oligomerization over the isomerization while less basic ones (PCl₃) slow down any reaction.

More detailed studies on the catalytic rearrangement of other lactones are presently in progress.

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