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HAMMETT-CORRELATIONS, SOLVENT EFFECTS AND STEREOCHEMISTRY OF THE THERMAL DECARBOXYLATION OF 2-OXETANONES - EVIDENCE FOR A ZWITTERIONIC INTERMEDIATE

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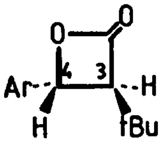
Summary: Kinetic and stereochemical data of the thermal decarboxylation of 2-oxetanones (1 and 2) indicate that the reaction proceeds via a zwitterionic intermediate Z.

The mechanism of the thermal decarboxylation of β-lactones (2-oxetanones) has received increasing attention during the past few years[1]. However, it has remained unclear so far, whether the reaction proceeds via a concerted mechanism or a zwitterionic intermediate Z. We wish to report that all the kinetic and stereochemical data we obtained from the decarboxylation of 1 and 2 are fully consistent with Z.



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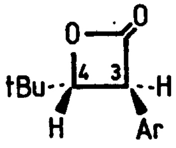

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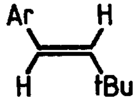

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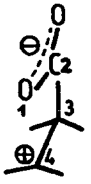


Z

1 and 2 were prepared from the corresponding threo-3-hydroxycarboxylic acids as described previously[2]. On thermolysis 1 and 2 are converted quantitatively into the same (E)-olefin 3. We determined the decarboxylation rates by means of ^{1}H-NMR-spectroscopy[3] and obtained first order rate laws for > 90% completion in all cases.

HAMMETT-Plots (Table 1). The substitution patterns of 1 and 2 are analogous though inverted with regard to the 3- and 4-positions. This ensures similar steric effects in 1 and 2 and renders these two lactone types particularly suited for a comparison of the electronic demands exerted on C-3 and C-4 respectively in course of the reaction. As the rate constants in Table 1 show, there is a remarkable difference between the ρ-values of 1 (ρ_1 = -3.39, σ^+-correlation[4], r = 0.993) and 2 (ρ_2 = +0.13, σ-correlation, r = 0.805). This indicates that in the transition state a considerable amount

Tab. 1 Rate Constants of the Thermolysis of trans-3-tert.-Butyl-4-aryl-2-oxetanones (1) and of trans-4-tert.-Butyl-3-aryl-2-oxetanones (2) in 1,2-Dichlorobenzene.

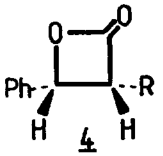
System	Ar	1 (50.0°C) 10^6k (s^{-1})	2 (160.0°C) 10^4k (s^{-1})
a	$p-N(CH_3)_2-C_6H_4-$	-	1.96
b	$p-OCH_3-C_6H_4-$	373	2.16
c	$p-CH_3-C_6H_4-$	1.89[a]	-
d	$m-CH_3-C_6H_4-$	-	2.11
e	C_6H_5-	0.182[b]	2.39
f	$m-Cl-C_6H_4-$	0.0121[c]	2.38
g	$p-CO_2CH_3-C_6H_4-$	-	3.23
h	$p-CN-C_6H_4-$	0.00 235[d]	-
i	$p-NO_2-C_6H_4-$	0.00 105[e]	-
j	4-pyridyl-	0.000 309[f]	-

The rate constants of 1 have been extracted from
100°C : ($3.30\cdot10^{-4}$ s^{-1})[a]; ($4.36\cdot10^{-5}$ s^{-1})[b]; 140°C : $1.61\cdot10^{-4}$ s^{-1})[c];
150°C : ($1.03\cdot10^{-4}$ s^{-1})[d]; ($5.60\cdot10^{-5}$ s^{-1})[e]; ($2.20\cdot10^{-5}$ s^{-1})[f]
using 1e as standard system (E_A = 26.2 kcal mol^{-1}; log A = 11.02).

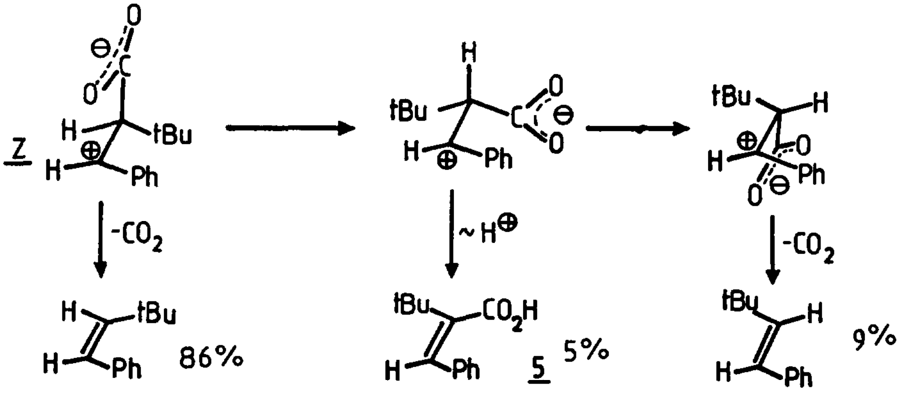
of positive charge is accumulated at C-4, whereas C-3 is practically indifferent towards the polar effect of the substituent attached to it[5]. In particular the magnitude of ρ_1, which is well in the range of typical S_N1/E1-values[6], strongly suggests that in the primary step of the decarboxylation a zwitterionic intermediate (Z) is generated. The formation of Z also provides a plausible explanation for the fact that, for analogous substituents, *1 reacts much faster than 2. So for 50.0°C the following ratios* are obtained: k(1f)/k(2f) = 27; k(1e)/k(2e) = 407; k(1b)/k(2b) = $8.3\cdot10^5$. The extremely large value in the last case can be easily explained by the efficient carbenium stabilization in the Z of 1b.

Solvent Effects. We determined the decarboxylation rates of 1e in the following solvents ($k\cdot10^4$ s^{-1} at 100.0°C) : decalin (0.0761), mesitylene (0.149), diphenylether (0.308), anisole (0.326), 1,2-dichlorobenzene (0.436), pyridine (1.10), HMPT (1.32), benzophenone (1.96), propylene carbonate (7.42), formanilide (33.3). A satisfactory correlation (r = 0.988) of the k-values with the E_T-parameters[7] is obtained. k (formanilide)/k (decalin) amounts only to 438; the solvent effect thus appears to be substantially lower than that found in S_N1/E1-processes[8]; however, we do not consider that as an argument against Z for the following three reasons: (1) for Z, which is tetramethylene species[9], strong <u>intramolecular</u> "through-space"-1.4-interactions have to be expected; thus the dipole moment of Z is certainly lower than that of the ion pairs encountered in an S_N1/E1-mechanism. (2) The reaction ß-lactone → olefin + CO_2 results in a considerable loss of overall polarity. Therefore, finding a positive solvent effect at all strongly suggests that a polar intermediate must be involved. (3) The abovementioned value of 438 is obtained at 100.0°C; an extrapolation to 25°C (the temperature of ref.8) results in a k (formanilide)/ k (decalin) of $\sim 10^3$.

<u>Stereochemistry.</u> If the reaction really proceeds via an open-chain intermediate like Z one might expect to some extent rotation around the C-3-C-4-axis and, in consequence, loss of stereochemistry. On the other hand, the abovementioned 1.4-interaction in Z tends to prevent such a rotation and to secure the retention of configuration[9]. Indeed, the <u>cis</u>-lactones <u>4</u> (R = CH_3, Et, iPr) all decarboxylate quantitatively to the corresponding (Z)-olefines with > 99% (GC-control) stereoselectivity. By contrast the Z which is generated from <u>cis</u>-<u>1e</u> suffers from a particularly high steric congestion and starts to rotate (Scheme 1); so in 1,2-dichlorobenzene at 140.0°C one obtains 86% <u>cis</u>-olefin and no less than 9% <u>trans</u>-olefin[10]. To our knowledge this is the first case of an <u>unstereospecific</u> decarboxylation of a ß-lactone. In addition to the two olefins <u>cis</u>-<u>1e</u> forms the acrylic acid <u>5</u>[11] which, as shown in Scheme 1, can easily be derived from Z by proton migration.


<u>4</u>

<u>Scheme 1</u>



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2) J. Mulzer, A. Pointner, A. Chucholowski, G. Brüntrup, J.Chem.Soc., Chem. Commun. 52 (1979) and cit. lit. The yields of 1 and 2 are between 78 and 95%; all our lactones have been fully characterized by IR- and ^{1}H-NMR-spectroscopy and give correct combustion analyses.

3) In recognition of the fact that ß-lactones are labile towards acid the NMR-tubes were treated with conc. ammonia for 24 hrs at 25°C, rinsed three times with water and dried at 80°C before use. The solvents were purified according to standard procedures (e.g. W. Bunge in Houben-Weyl-Müller, Methoden der Organischen Chemie, Vol.I/2, p.765, Thieme, Stuttgart, 1959) followed by either filtration over Al_2O_3 and distillation or distillation over CaH_2 (in vacuo). All 2-oxetanones were recrystallized several times from pentane. The kinetic runs were performed in 10 mole % solution and evaluated by setting the intensity of one proton in lactone + olefin = 100%. The accuracy of the rate constants is about ± 5%.

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