EQUILIBRIUM CONSTANTS, DIFFERENTIAL RESONANCE ENERGIES, AND ACID PROPERTIES OF THE HYDROXY FORMS OF TAUTOMERIC 2-THIAZOLONE – 2-HYDROXYTHIAZOLE AND 2-PYRIDONE – 2-HYDROXYPYRIDINE SYSTEMS

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2-Thiazolone exists in solution in equilibrium with a small amount of the hydroxy form, the percentage of which is beyond the limits of the possibility of determination by IR and UV spectroscopy. We calculated $pK_t = -\log$ [hydroxy form]/[oxo form] of this equilibrium using the Ebert method [1] and the ionization constants (addition of a proton) of fixed methyl modles of the tautomers. The pK_a^{20} values* of 3,4-dimethyl-2-thiazolone (−1.70 ± 0.05) [2] and 2-methoxy-4-methylthiazole (2.22 ± 0.03) [2] were used in the calculation. The pK_t^{20} value for the 2-thiazolone–2-hydroxythiazole system was found to be 3.92 ± 0.08; the pK_t^{20} value for the 2-pyridone–2-hydroxypyridine system was found to be 2.53 ± 0.07 [3]. Consequently, replacement of the −CH=CH− grouping by a sulfur atom decreases the relative percentage of the hydroxy form by more than one order of magnitude. The difference between the resonance energies of 2-hydroxy-4-methylthiazole and 4-methyl-2-thiazolone was calculated by the Katritzky method, in which it is set equal to $\Delta Gu - \Delta Gs$, calculated from the pK_a values of the six methyl models of the tautomers. The pK_a values for the addition of a proton to 2-methoxy-4-methylthiazole and 3,4-dimethyl-2-thiazolone cited above, the $pK_a^{25°}$ value† of 2-methyl-Δ^2-thiazoline (5.37 ± 0.06) [5], and our measured value* (−2.11 ± 0.10; H_A) for 2-thiazolidinone ($\Delta Gu - \Delta Gs = 4.79 \pm 0.32$ kcal/mole) were introduced in the calculations. On passing from the 2-hydroxy to the 2-oxo form the loss in resonance energy for the thiazole system is 15%,‡ as compared with 23% for the pyridine system [4]. Thus the conversion to the oxo form for the pyridine system leads to a greater loss of resonance energy than for the thiazole system, and in the first case the percentage of the 2-hydroxy form, which is richer in this energy, is higher. The rather high degree of aromatic character of 2-thiazolone correlates with its ability to readily undergo substitution at the carbon atom with weak electrophiles ($Ac_2O \cdots H^+$, $Me_2\overset{+}{N}=CH-$), which we have previously observed [6].

The pK_t^{20} values for the given tautomeric system, the pK_a^{20} value† for splitting out of a proton from 2-pyridone (11.62 ± 0.03) [3], and our previously determined pK_a^{20} value† for 4-methyl-2-thiazolone (10.65 ± 0.03) [7] enabled us, by means of the prototropic tautomerism equation [8], to calculate the pK_a^{20} values of 2-hydroxypyridine and 2-hydroxythiazole, which were 9.09 ± 0.10 and 6.73 ± 0.11, respectively. The high acidities of these compounds as compared with phenol (pK_a^{20}‡ = 9.98 ± 0.03 [9]) constitute evidence that the additional driving force of their protonation is the inductive effect of the N=COH nitrogen atom and the $S\text{-}\overset{\|}{C}OH$ sulfur atom.

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*By a spectrophotometric method.

†By a potentiometric method.

‡The value of 4.79 ± 0.32 kcal/mole was compared with the resonance energy of pyridine [4] (32 kcal/mole) because of the lack of data on the resonance energy of thiazole.

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REACTION OF 1,3-DIOXEPANE WITH ETHYL ACETATE

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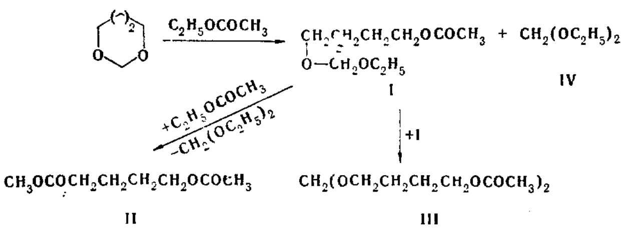
In a search for a reagent capable of cleaving cyclic formals at one of the ring C−O bonds to give a stable intermediate, we studied the reaction of 1,3-dioxepane with ethyl acetate [in a glass thermostatted reactor at 70°, a 1,3-dioxepane to ethyl acetate ratio of 1 : 2, 1% (of the charge) H_2SO_4 as the catalyst, and a reaction time of 3 h]. The primary reaction products – 5,7-dioxa-1-nonanol acetate (I) – and 1,4-butanediol diacetate (II), 5,7-dioxa-1,11-undecanediol diacetate (III), and diethoxymethane (IV) were isolated by means of preparative gas–liquid chromatography (GLC) (PAKhV-05, Apiezon L on Chromaton N-AW, at 160-220° and a helium flow rate of 12 liters/h). On the basis of a determination of the kinetic parameters, a separate study of the reaction of I with ethyl acetate, and its behavior in the absence of the ester, the most probable scheme for the formation of the isolated compounds is as follows:



The observed formation of unsymmetrical I and symmetrical III – linear formals that contain an ester group – is specific for 1,3-dioxacyclanes. Compounds of this sort cannot be obtained in the case of linear formals or oxygen-containing heterocyclic compounds with oxygen atoms separated by more than one carbon atom. Compound I, with bp 116° (6 mm), n_D^{20} 1.4390, and d_4^{20} 1.0350, was obtained in 21.1% yield. Compound II, with bp 225°, n_D^{20} 1.4189, and d_4^{20} 1.0620, was obtained in 48.6% yield. Compound III, with bp 147° (8 mm), n_D^{20} 1.4640, and d_4^{20} 1.1012, was obtained in 12.8% yield. The mass spectra of I and III contain CH_3CO^+ ions (m/e 43, 100%). The ^{13}C NMR spectra contain signals of CH_3 groups at 21.1-22.1 ppm and a singlet at 169.1-169.4 ppm (COO^-); the methyl groups resonate at 61.2-64.5 and 68.6-68.8 ppm, depending on the environment.

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