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STRUCTURAL COURSE OF THE SCISSION OF 2,4-DIMETHYL-1,3-DIOXALANE BY ACETYL CHLORIDE

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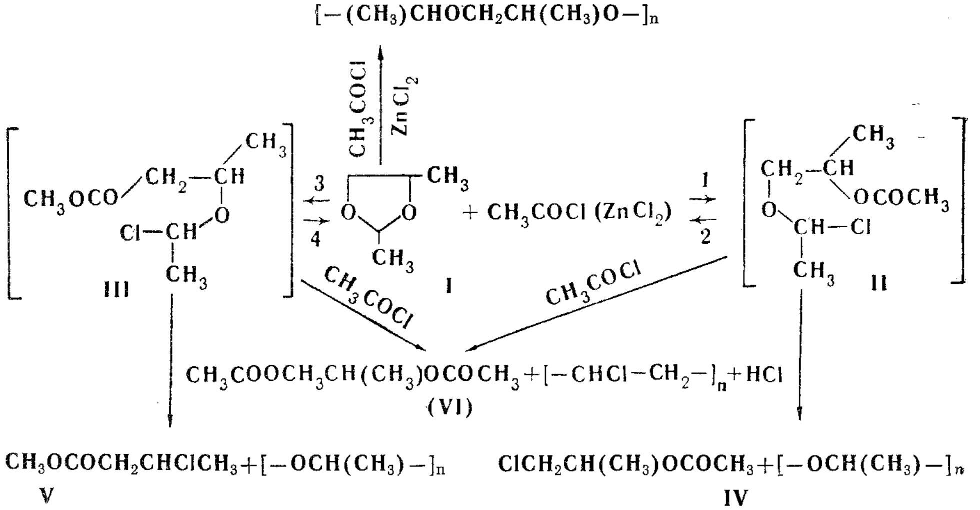
The reaction of 2,4-dimethyl-1,3-dioxolane with acetyl chloride in the presence of $ZnCl_2$ catalyst gives only one of two expected chloropropylacetates (the 2-chloropropylacetate), along with propylene glycol diacetate, and resinous products, formed by splitting of the intermediate α-chloroesters, as well as by polymerization of the starting dioxolane. IR spectra confirmed the structure of the 2-chloropropylacetate. An attempt is made to explain the structural course of the reaction.

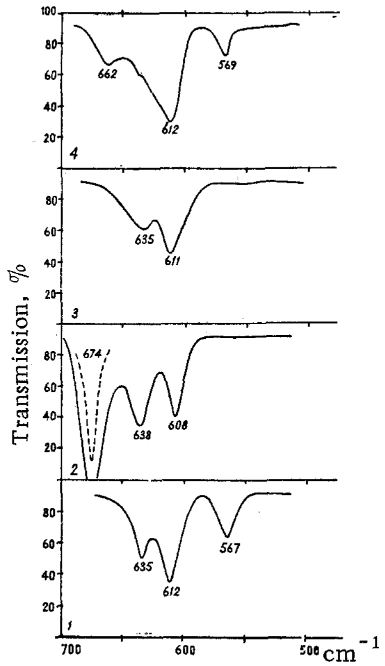
Continuing our research on the mechanism of the scission of the dioxolane ring by acyl halides [1], we have investigated the reaction of 2, 4-dimethyl-1,3-dioxolane (I) with acetyl chloride in the presence of catalytic amounts of $ZnCl_2$. The equation previously put forward [1] would lead one to expect, under those conditions, formation of both 2-chloroisopropylacetate (IV), and 2-chloro-n-propylacetate (V), along with the diacetate (VI), and tarry products, formed by decomposition of the intermediate α-chloroesters II and III, and by polymerization of the starting dioxolane.



... (1)

However, gas-liquid chromatography (GLC) shows that over-all only one of the possible β-chloroesters is formed, and by IR spectroscopy it could be established that this was 2-chloropropylacetate V. Comparing its spectrum (figure, plot 1) with the spectra of β-chloroethylacetate (plot 2) and n-propylacetate (plot 3), it can be seen that the bands at 635 and 612 cm^{-1} are due to the OCOMe group, while the presence of the C–Cl link gives rise to bands at 567 and 674 cm^{-1} (and correspondingly for the chloroester under investigation, and β-chloroethylacetate). From the present results, and in agreement with what has been published [2,3], the 674 cm^{-1} band is to be related to C–Cl at the primary carbon atom. The ν 567 cm^{-1} band, generally characteristic of a C–Cl link with an enhanced chlorine atom mobility (e.g., tertiary chlorine in alkyl halides [2,3]), must be ascribed to vibrations of a chlorine atom at a secondary carbon atom in the compound under investigation, since the equation does not allow formation of an isomer with a tertiary chlorine atom, $Me_2CClOAc$. Further, the chemical properties of the latter correspond to those of an α-chloroester, so that it cannot be mistaken for its isomer V. The observed decrease in chlorine vibration frequency at a secondary carbon atom as compared with alkyl halides, is firstly to be ascribed to the cooperative effects of a methyl group and an acetoxy group, increasing the chlorine atom frequency, and secondly, by the extreme sensitivity of the C–Cl link to change in the skeleton of the molecule.

The structural course of the reaction investigated can be explained on a basis of an analysis of the equilibrium system, shown in the diagram. Reaction 1, giving the intermediate α-chloroester II (which may decompose to give 2-chloroisopropylacetate IV), should be repressed through simultaneous action of a number of factors: 1) hindrance to formation of acetate of a secondary alcohol in comparison with that of a primary one [4]; 2) the rate of the reverse cyclization 2 should be greater than that of the rate of the cyclization 4 due to the much higher electron density at the ester oxygen atom of the acetoxy group in compound II; 3) as compared with compound II, compound III is energetically more advantageous, since the fractional positive charge, arising at the appropriate carbon atom at position 4, is partly extinguished by the electron-pumping (electron-giving) methyl group. On the other hand, in compound II, the positive charge at the similar carbon atom 5 is more localized, due to its not having an electron-donating substituent on it; 4) the initial electrophilic attack due to the shielding action of the methyl groups must be mainly directed to oxygen atom 1.



IR spectra: 1) 2-chloropropylacetate; 2) 2-chloroethylacetate; 3) n-propylacetate; 4) mixture of two isomers of chlorobutylacetate (IKS-14, spectrometer, KBr prism).

Hence it is to be expected that with increased distance along valence bonds between the α-chlorine atom and the acyl group, the difference between the cyclization velocities of α-chloroesters of types II and III will decrease. This will increase the probability of formation of the isomer with a primary chlorine atom. In point of fact, a mixture of two isomeric γ-chlorobutylacetates was isolated from the products of reaction of the cyclic acetal of 2,4-dimethyl-1,3-dioxane with acetyl chloride.

Spectrum analysis showed that in accordance with the view put forward above, the predominant isomer is a γ-chlorobutylacetate with a secondary chlorine atom, ($MeCHClCH_2CH_2OAc$).

In the IR spectrum of the mixture of isomers obtained (figure, plot 4), the ν 569 cm^{-1} band was found, but in addition there appeared a band at ν 660 cm^{-1}, corresponding, as was shown above, to C—Cl vibrations in the primary group.

Experimental

Reaction of 2,4-dimethyl-1,3-dioxolone (I) with acetyl chloride. When 25.5 g (0.25 mole) I, comprising 36% trans and 64% cis isomer (GLC analysis) was mixed with 0.1 g $ZnCl_2$ and 19.6 g (0.25 mole) AcOCl, evolution of heat was observed, and the temperature rose to 50° C. The mixture was stirred for 3 hr at that temperature, then distilled, to give, along with unchanged starting material, and tarry residue (2.2 g), two fractions, corresponding to the chloropropylacetates IV, V, and 1,2-propylene glycol diacetate VI. To decompose traces of α-chloroesters II, III was extracted with water, dried over Na_2SO_4, and repeatedly distilled. Yield 11.1 g V (32.5%), bp 66°–67° C (33 mm), n_D^{20} 1.4223; d_4^{20} 1.0914. Found: C 43.79, 43.53; H 6.74, 6.29%. Calculated for $C_5H_9ClO_2$: C 43.79; H 6.57%.

2,4-Me_2-1,3-dioxolane was reacted similarly with AcOCl, to give mixed chlorobutylacetates bp n_D^{20} 1.4299; d_4^{20} 1.0666. Found: C 47.63; H 7.11%. Calculated for $C_7H_{11}ClO_2$: C 47.61; H 7.30%.

GLC analysis was carried out with a LKhM-5 instrument, SKB IOKh, AN SSSR system. Conditions: temperature 80° C, carrier gas He, 60 ml/min, column 4 m long, 5 mm diameter, support NaCl, 0.1–0.25 mm; liquid phases a) di-n-heptylsebacate; b) polyethylmethylsiloxane still residue, 1% on weight of support. The materials analyzed comprised a cut corresponding to chloropropylacetate, and the total reaction product without previous rectification. Chlorobutylacetate separation conditions: temperature 100° C, carrier gas helium, 60 ml/min, column 4 m long, NaCl carrier, 0.1–0.26 mm, liquid phase di-n-heptylsebacate, 1% by weight on the support.

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