INVESTIGATIONS IN THE FIELD OF VINYL ETHERS AND ESTERS OF THE FURAN SERIES

I. Synthesis of the Vinyl Ester of α-Furancarboxylic Acid and Some of Its Reactions

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Vinyl α-furancarboxylate has been synthesized by the reaction of α-furancarboxylic acid with acetylene and with vinyl acetate in the presence of various catalysts. The structure of the vinyl ester has been confirmed by IR spectra and by catalytic hydrogenation. The acid and alkaline hydrolyses of vinyl α-furancarboxylate have been studied.

Derivatives of α-furancarboxylic acid (I) are widely used in industry and medicine. We felt it was of interest to synthesize and study the properties of the vinyl ester of α-furancarboxylic acid (II). The possibility of its synthesis by the direct vinylation of I at 225–230° C is mentioned in the literature [1]. The yield of vinyl ester is not given.

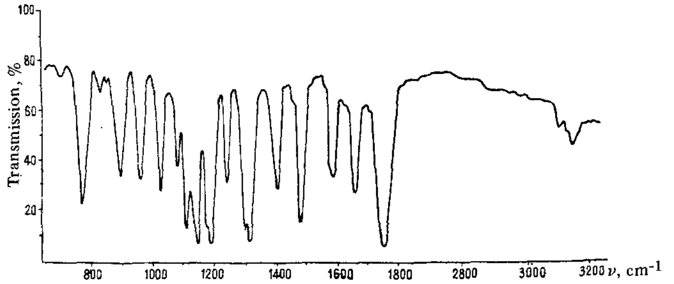
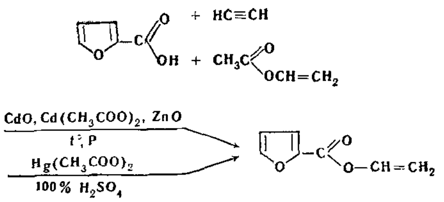


Fig. 1. IR spectrum of II.

In the present work, we have studied the reaction of I with acetylene under pressure in the presence of such catalysts as cadmium acetate, zinc oxide, and cadmium oxide. The reaction was studied at various temperatures. The best yield of II, amounting to 74%, was obtained from 0.05 mole of cadmium oxide per mole of I in dioxane with heating to 165–170° C for half an hour. Under the same temperature conditions, in the vinylation of I in the presence of zinc oxide the yield of II amounted to 49% of theory, and in the presence of $Cd(CH_3COO)_2$ it was only 10–15%. When the process was carried out without a solvent or at a higher temperature, the yield of II fell because of the resinification of the reaction products. The same result was observed when the reaction time was increased from 1 to 2 hr. Under the optimum conditions found, the reaction of I with acetylene takes place mainly in the following way:



As can be seen from the scheme, we also obtained II by the reaction of I with vinyl acetate. It was found that in an excess of vinyl acetate at 20° C under the action of mercury acetate with the addition of concentrated sulfuric acid, the yield of II in 72 hr amounted to 47.5%. Thermostatting the reaction mixture at 25–60° C promoted the resinification of the starting materials and the reaction products.

Vinyl α-furancarboxylate is a colorless liquid soluble in ethanol, acetone, dioxane, and carbon tetrachloride. Its structure was confirmed by the results of infrared spectroscopy and also by its hydrolytic cleavage and catalytic hydrogenation reactions. The IR spectrum of II is given in Fig. 1. The terminal double bond adjacent to the oxygen atom can be identified from the strong absorption band at 1650 cm^{-1} and from the weak frequencies in the 3100 cm^{-1} region. These bands disappear in the hydrogenation product of II [2].

The acid hydrolysis of II was studied in most detail at 96–98° C as a function of the time of heating and the concentration of the sulfuric acid. The results obtained are shown graphically in Fig. 2. It was established that the degree of hydrolysis of the II rises linearly with an increase in the time of heating from 0.5 to 4 hr in the presence of 2% H_2SO_4 (curve 1), while in the presence of more concentrated acid (curve 2) it passes through a maximum. The yield of acetaldehyde reaches 93% after 3 hr and then falls, which can apparently be explained by the resinification of the reaction products. The acidity of the medium strongly influences the degree of hydrolysis. The dependence of the hydrolytic cleavage of II on concentration of sulfuric acid is shown by curve 3. A fall in the reaction temperature to 60° C led to a marked decrease in the yield of acetaldehyde, to approximately 5–6%. At 20° C, II undergoes practically no hydrolysis in 3 hr in the presence of 5% H_2SO_4. This showed that the vinyl ester II hydrolyzes quantitatively under considerably more severe conditions than the vinyl ethers of furan

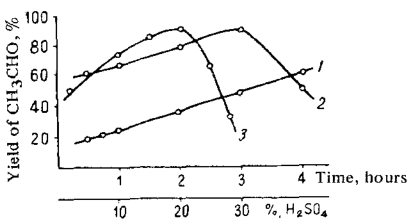


Fig. 2. Acid hydrolysis of II as a function of the time of heating and the concentration of sulfuric acid (for the identification of the curves, see text).

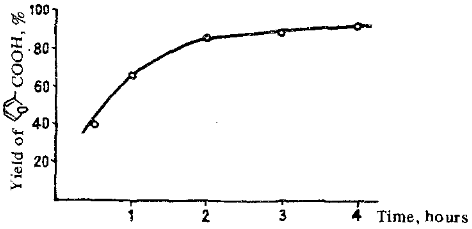


Fig. 3. Degree of hydrolysis of II as a function of the time of the reaction.

alcohols [3,4]. Under the influence of dilute alkaline solutions, the vinyl ester II readily undergoes saponification even at 20° C with the formation of the I. The degree of cleavage of II as a function of the time of this reaction is shown in Fig. 3.

The addition of hydrogen to the double bond of the vinyl group of the ester II takes place readily under the influence of a Raney nickel catalyst at room temperature with the formation of the known ethyl α-furancarboxylate.

The initial acid I was synthesized from furfural by a method analogous to that described for the preparation of 5-chloro-α-furancarboxylic acid from 5-chlorofurfural [5].

EXPERIMENTAL

α-Furancarboxylic acid (I). With cooling to 10° C, 74.2 g (0.77 mole) of furfural was added to 400 ml of a solution of sodium hypobromite obtained from 32 ml of bromine, 78 g of NaOH, and 350 ml of water, and the reaction mixture was stirred for 4 hr. The acid was isolated by the addition of small portions of concentrated hydrochloric acid until the I ceased to precipitate. It was filtered off and dried to constant weight. This gave 68 g (91%) of I, which was crystallized from water, mp 133° C [6].

Vinyl α-furancarboxylate (II). a) Vinylation of I. A 2-liter rotating steel autoclave was charged with 105 g of I, 6 g of cadmium oxide, and 180 g of dioxane. Acetylene was passed in from a cylinder under pressure of 12–15 atm. The contents of the autoclave were heated at 165–170° C for 40 min, cooled, and filtered, and the dioxane was distilled off under reduced pressure. The residue was distilled in vacuum in a current of nitrogen to give 95.34 g of the ester II, bp 71–72° C (10 mm) d_4^{20} 1.1472, n_D^{20} 1.5070. Found, %: C 60.81; H 4.28; MR_D 35.82. Calculated for $C_7H_6O_3$, %: C 60.86; H 4.38; MR_D 34.22.

b) Reaction of I with vinyl acetate. A mixture of 11.2 g (0.1 mole) of the acid I and 51.6 g (0.6 mole) of freshly-distilled vinyl acetate was carefully stirred. Then 0.23 g of mercury acetate, 0.6 g of 100% H_2SO_4, and 0.05 g of hydroquinone were added. The reaction products were thermostatted at 20° C for 3 days. After this, 1.35 g (0.12 mole) of sodium acetate was added. The precipitate was filtered off and the excess of vinyl acetate and the acetic acid formed in the reaction were eliminated. The yield of the ester II was 6.52 g, bp 51–52° C (4 mm).

Ethyl α-furancarboxylate (III). A hydrogenation vessel was charged with 2.16 g of II, 15 ml of absolute ethanol, and Raney nickel catalyst. Hydrogen was fed in from a gasometer at 20° C. A total of 0.39 *l* of gas was absorbed. The theoretically-required amount is 0.38 *l*. This gave III with mp 34° C [7]. Yield 90%.

Acid hydrolysis of the ester II. A 0.1190 g sample of the vinyl ester II was placed in a 50-ml tube containing 20 ml of 20% H_2SO_4. The sealed tube was heated at 96–98° C for 3 hr. The acetaldehyde was determined by Ripper's method—by the addition of a solution of sodium bisulfite to the reaction mixture and back-titration of the excess with 0.1 N iodine solution [8]. The percentage hydrolysis was 92.97. Experiments under other reaction conditions were carried out similarly. The results are given in the form of curves in Fig. 2.

Alkaline hydrolysis of II; In a conical flask, 0.2091 g of II was treated with 19.4 ml of 0.1 N NaOH. The mixture was left to stand in a thermostat at 20° C for 4 hr. The excess of alkali was back-titrated with 5.6 ml of 0.1 N HCl in the presence of Phenol Red. The yield of the acid I was 91.4%. The results obtained after 0.5, 1, 2, 3, and 4 hr are given in Fig. 3.

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