INVESTIGATIONS OF VINYL ESTERS OF THE FURAN SERIES

X.* SYNTHESIS AND SPECTRAL INVESTIGATION OF VINYL ESTERS OF FURAN-2-CARBOXYLIC ACIDS

G. G. Skvortsova, V. V. An,
Yu. A. Mansurov, V. K. Voronov,
G. V. Ratovskii, and Yu. L. Frolov

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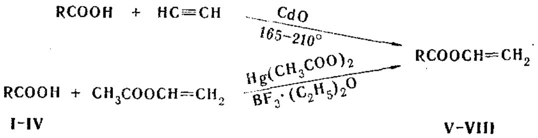
The vinyl esters of trans-β-(2-furyl)acrylic acid, furan-2-carboxylic acid, 5-bromofuran-2-carboxylic acid, and 5-nitrofuran-2-carboxylic acid were synthesized by the reaction of the corresponding acids with acetylene and vinyl acetate. Mercuric acetate and boron trifluoride etherate were used as catalysts for the transvinylation of acids of the furan series. The structures of the vinyl esters obtained were proved by IR and PMR spectroscopy. The distribution of the π-electron density in the molecules of four of the synthesized vinyl and ethyl esters was studied by means of quantum-chemical calculations by the SCF MO LCAO method (Pople variant) using the Raman and UV absorption spectra.

The synthesis of vinyl esters of furan-2-carboxylic acid and 5-bromofuran-2-carboxylic acid by direct vinylation using zinc [2] and cadmium [3] oxides as the catalysts and also by transvinylation of the acids with vinyl acetate in the presence of mercuric acetate and sulfuric acid [3,4] is well known. The amount of study devoted to the properties of the vinyl esters of acids of the furan series has been extremely inadequate. In addition, only very brief and contradictory patent data [5,6] on the reaction of unsaturated acids with acetylene are available in the literature. In this connection, it seemed of interest to us to work out methods for the preparation of new vinyl monomers of the furan series for the investigation of the reaction of 5-bromofuran-2-carboxylic acid and 5-nitrofuran-2-carboxylic acid (I and II) and trans-β-(2-furyl)acrylic acid (III) with acetylene and vinyl acetate, to compare these methods with the conditions for the vinylation of furan-2-carboxylic acid (IV), and to study the peculiarities of the IR and PMR spectra of the vinyl esters obtained (V-VIII). In the present study we have also attempted to examine the peculiarities of the intramolecular interaction in esters V-VIII using data from the Raman and UV absorption spectra.

The vinyl esters of acids of the furan series were synthesized via the following scheme:



IV, V R 2-furyl I, VI R = 5-bromo-2-furyl
II, VII R = 5-nitro-2-furyl; III, VIII R= β-(2-furyl)vinyl

The reaction of acids I-III with acetylene under pressure was investigated while varying the reaction temperature from 160 to 220°C in the presence of cadmium oxide (0.05 mole of CdO per mole of acid). Under these conditions and with heating in dioxane for 30-40 min, acids with electronegative substituents in the 5 position of the furan ring (I, II) are vinylated with greater difficulty than acid IV [3]. Thus, VI and VII are obtained in optimum yields (45 and 10%, respectively) at 180-185° and 205-210°. Acid IV forms ester V

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*See [1] for communication IX.

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TABLE 1

$RCOOCH{=}CH_2$

Comp.	R	bp, °C, mm	n_D^{20}	d_4^{20}	MR_D		Empirical formula	Found, %		Calc., %		Yield, %	
					found	calc.		C	H	C	H	A	B
V	Furyl	71 (10)*	1,5070	1,1472	35,82	34,22	$C_7H_6O_3$	60,8	4,3	60,9	4,4	74,0	50
VI†	5-Bromo-2-furyl	94 (5)	1,5460	1,5647	43,90	42,00	$C_7H_5BrO_3$	38,8	2,5	38,7	2,3	44,7	55,1
VII	5-Nitro-2-furyl	90	—	—	—	—	$C_7H_5NO_5$	46,0	2,7	45,9	2,8	10,0	78,7
VIII	β-(2-Furyl)-vinyl	90 (4)	1,5835	1,1165	49,16	42,99	$C_9H_8O_3$	65,9	4,8	65,9	4,9	33,4	60,3

*Bp 70-73° (10) [2].

†Bp 87° (4), n_D^{20} 1.5457, d_4^{20} 1.562 [4].

‡This is the melting point.

TABLE 2. IR Spectral Data and Chemical Shifts of the Protons of the Vinyl Group of Vinyl Esters V-VIII

Comp.	Frequencies of the absorption band maxima, cm^{-1}			δ, ppm*		
	C=O	$CH{=}CH_2$	furan	α	β	β′
V	1750	3100, 1650, 952	3145, 3125, 1580, 886, 763	7,38	4,59	4,94
VI	1730	3098, 1650, 945	3155, 3130, 1575, 875, 750	7,35	4,63	4,96
VII	1752	3110, 1650, 954	3150, 1590, 890, 764	7,36	4,76	5,12
VIII	1728	3095, 1638, 950	3155, 3130, 1558, 885, 750	7,34	4,48	4,84

*$J_{\alpha\beta'} \simeq 14$ Hz, $J_{\alpha\beta} \simeq 6$ Hz, $J_{\beta\beta'} \simeq 1.5$ Hz.

in high yield (74%) with acetylene at 165-170°. Acids I and II do not react at all with acetylene at this temperature, and the starting materials are completely recovered. Acid III undergoes 30-35% vinylation at 160-170°. We were unable to attain a higher degree of conversion of acid III to ester VIII under these temperature and catalytic conditions. An increase in the duration of heating of this reaction mixture promotes a decrease in the yield of VIII due to resinification and polymerization of both the starting acid (III) and the resulting ester.

Vinyl esters V-VIII were also synthesized by transvinylation. This reaction is usually carried out in the presence of mercuric acetate in sulfuric acid [7]. In the transvinylation of acids I-IV, we used boron trifluoride etherate [8] in place of sulfuric acid; the etherate was relatively recently used for the synthesis of vinyl esters of unsaturated acids [9, 10]. As a result of the investigations, we established that acids I-IV react with vinyl acetate under the influence of mercuric acetate and boron trifluoride etherate at 20-60° in the course of 0.5-1 h to give esters V-VIII in 50-80% yields. This method [11] differs favorably from the method in [7], in which a sixfold excess of vinyl acetate is necessary for the synthesis of the vinyl esters, and the process takes 72-77 h. It is presently supposed that transvinylation in the presence of sulfuric acid and mercuric acetate proceeds via an ionic mechanism with the formation of mercury-containing compounds [12]. In our investigations of the transvinylation of acids I-IV, in which H_2SO_4 is replaced by boron trifluoride etherate, the etherate apparently acts as a strong acid and promotes the dissociation of $Hg(CH_3COO)_2$ and splitting out of an acetyl group.

Compounds V, VI, and VIII are colorless transparent liquids, while VII is obtained as light-yellow crystals with mp 90° (Table 1). All of the compounds are insoluble in water but are quite soluble in organic solvents. The structures of the esters were proved by IR and PMR spectroscopy. There are strong absorption bands at 1635-1650 cm^{-1}, which correspond to the stretching vibrations of the $-C{=}C-$ group in the vinyloxy grouping and the acrylic fragment of the acid [13, 14], in the IR spectra of all of the investigated esters (Table 2). The terminal double bond adjacent to an oxygen atom can also be identified from the bands at 945-955 and 3100 cm^{-1}.

The PMR spectra which confirm the structures of V-VIII are presented in Fig. 1. In the spectrum of V, the signal of the 3-H proton is represented by a doublet, 4-H is represented by a quartet, and 5-H is represented as a broad singlet (δ_3 7.21, δ_4 6.48, δ_5 7.61 ppm: $J_{34} \simeq 3.5$ Hz, $J_{45} \simeq 1.5$ Hz). In substituted furans [15], one usually observes that $J_{34} > J_{45} > J_{35}$. The fine structure of the 3-H and 4-H signals is therefore resolved in the spectrum, while the 5-H signal is only appreciably broadened. The introduction of a bromine atom into the 5 position of the furan ring has practically no effect on the position of the signals of the 3-H and 4-H protons which are represented in the PMR spectrum of VI as doublets with a

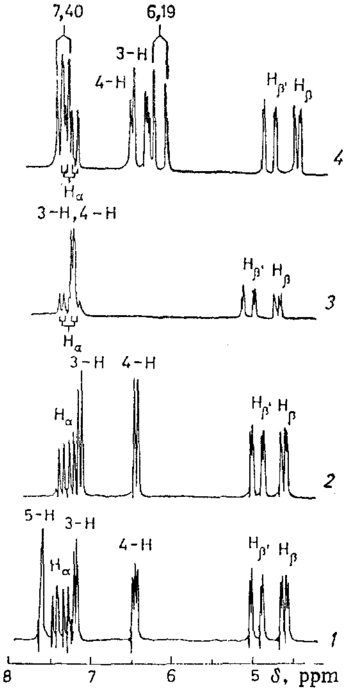

Fig. 1

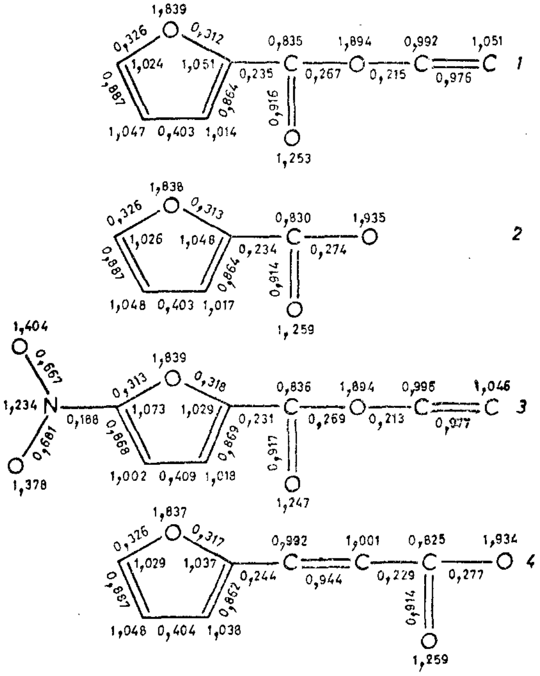

Fig. 2

Fig. 1. PMR spectra of vinyl esters V-VIII: 1) vinyl furan-2-carboxylate (V); 2) vinyl 5-bromofuran-2-carboxylate (VI); 3) vinyl 5-nitrofuran-2-carboxylate (VII); 4) vinyl trans-β-(2-furyl)acrylate.

Fig. 2. Diagrams of the distribution of the π-electron density for molecules of vinyl esters (V, VII) and ethyl esters of acids I and IV: 1) vinyl furan-2-carboxylate (V); 2) ethyl furan-2-carboxylate; 3) vinyl 5-nitrofuran-2-carboxylate (VII); 4) ethyl β-(2-furyl)acrylate.

rather large ($\simeq 20$) $(\delta_3 - \delta_4)/J_{34}$ ratio. On the other hand, the nitro group in VII has a substantial effect on the position of the 4-H signal in that it reduces the $(\delta_3 - \delta_4)$ difference. The protons of the CH=CH group in the PMR spectrum of VIII gave two doublets (δ 7.70 and 6.19 ppm) with a J constant of 15 Hz; this indicates a mutual trans orientation. This fact is evidence that the configuration of the molecules is not disrupted in the vinylation of the trans acid (III), and the trans ester (VIII, Table 2) is obtained. The remaining signals in the spectra of V-VIII are caused by the protons of the vinyl group (Table 2). The position of these signals in the PMR spectra is characteristic for vinyl esters and is determined by conjugation of the oxygen with the double bond [15]. Attention is directed to the fact that the values of the signal of the proton in the α position in the PMR spectra practically coincide for all of the compounds. The chemical shifts of the protons attached to the β carbon atom in the spectra of V and VI differ appreciably from δ_β and $\delta_{\beta'}$ in the spectra of VII and VIII. This is evidence for different contributions of the resonance structures in these compounds; the structures reflect the conjugation of the oxygen with the double bond [15]. The introduction of a nitro group into the 5 position of the furan ring has the most appreciable effect on the electronic structure of the vinyl group and of the entire molecules.

Diagrams of the distribution of the π-electron density are presented in Fig. 2 for molecules of vinyl compounds V and VII and alkyl esters of acids III and IV; the values were calculated by the Pople variant of the SCF MO LCAO method. According to these data, the furan ring, the furylvinyl grouping, and the ether oxygen give rise to a donor effect with respect to the carbonyl group. The introduction of a vinyl grouping attached to an oxygen atom leads to an additional decrease in its electronic charge, and one observes a rather weak decrease in the electronic charge on the carbonyl group and a somewhat more pronounced change in its polarity. A nitro group in the 5 position of the furan ring has only a slight weakening influence on the donor effect of the furan ring with respect to the carbonyl group and leads to a reduction in the polarity of the C=O and C=C bonds. These investigations have demonstrated that weak competitive interactions between the structural groups are characteristic for the ground state.

EXPERIMENTAL

Synthesis of Esters of I-IV (V-VIII, Tables 1 and 2). A. A rotary steel autoclave was charged with 0.47 mole of the appropriate acid (I-IV), 3 g of cadmium oxide, and 100 ml of dioxane. Acetylene was fed into the autoclave from a cylinder under a pressure of 12-15 atm. The contents of the autoclave were heated at 165-210° for 40 min. In the case of I, II, and III, the temperature was 180-185°, 205-210°, and 165-170°, respectively. The mixture was cooled and filtered, and the dioxane was removed from the filtrate by distillation. Compounds V, VI, and VIII were vacuum distilled in a stream of nitrogen, while VII was crystallized from alcohol.

B. A mixture of 0.044 mole of the appropriate acid (I-IV), 20 ml (0.21 mole) of vinyl acetate, 1 g of mercuric acetate, 0.1 ml of boron trifluoride etherate, and traces of hydroquinone was stirred at 20-60° for 0.5-1 h (for I, II, III, and IV, the temperature was 20°, 60°, 30°, and 40°, respectively). The resulting esters (V-VIII) were isolated as described above.

The PMR spectra of CCl_4 solutions of the compounds were recorded with a JNM-4H-100 spectrometer at room temperature with hexamethyldisiloxane as the internal standard. The IR spectra of V, VI, and VIII (in a microlayer) and of VII (KBr pellet) were recorded with a UR-20 spectrophotometer.

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