REACTIONS OF ALDEHYDES OF THE FURAN SERIES

I. NEW METHOD FOR THE PREPARATION OF 1,2-DI-(2-FURYL)ETHYLENE DERIVATIVES

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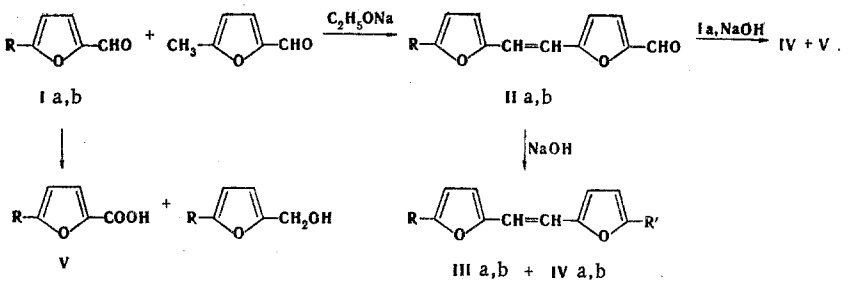
UDC 547.724.727:543.422.4.6'51

The lability of the hydrogen atoms in the methyl group of 5-methylfurfural was proved by a reaction of the crotonic condensation type. Aldehydes, alcohols, and acids of the 1,2-di(2-furyl)ethylene series were synthesized. The optimum conditions (reagent ratio, elevated temperatures, catalysis by sodium ethoxide) that make it possible for the condensation process to prevail over side reactions were selected. The Cannizzarro reaction that accompanies condensation is the reason for the accumulation in the reaction mixture of furfuryl alcohols and furancarboxylic acids. Aldehydes of the 1,2-di-(2-furyl)ethylene series also participate in this reaction, on the basis of which it is proposed that alcohols and acids of this series be obtained by this method.

The problem of the lability of the hydrogen atoms in the methyl group of 5-methylfurfural has not previously been posed in the literature, whereas data on the mutual effect of substituents in the 2 and 5 positions of the furan ring [1, 2] make it possible to assume that this lability is real. We have obtained confirmation of this assumption on the basis of a reaction of the crotonic condensation type. We examined the possibility of the reaction of 5-methylfurfural with furfural (I) in order to develop a practical method for the preparation of 1,2-di(2-furyl)ethylene derivatives [aldehydes (II), acids (III), and alcohols (IV) with a functional group in the α position of the furan ring]. Syntheses of 1,2-di(2-furyl)ethylene itself by decomposition of furfural azine [3], by the Wittig reaction [4], and from acetylenic derivatives of carboxy compounds [5] are known.

A search for conditions that ensure condensation showed that catalysis by KOH or NaOH in water and in alcohol leads primarily only to Cannizzarro reaction of the starting aldehydes. However, substances whose UV spectra in the long-wave region (330-360 nm) indicate the presence of a conjugated polyene system can be obtained in small amounts in this case.



I–V a R=H; b R=CH_3; III R′=COOH; IV R′=CH_2OH

Catalysis by sodium ethoxide in various absolute solvents at 60-70°C was found to be optimal in the synthesis of 1,2-difurylethylenes. Elevated temperatures ensure accelerated condensation up to the point where the water liberated as a result of the reaction converts the ethoxide to sodium hydroxide. The process can be directed to form the aldehyde or acid and alcohol of the 1,2-di(2-furyl)ethylene series by changing the amount of ethoxide. At low ethoxide concentrations (0.1-0.2 mole per mole of the sum of the reacting aldehydes) the reaction leads to aldehyde II in 80-95% yield. However, if the ethoxide is taken in amounts ranging from 0.6 to 0.8 mole per mole of furan aldehydes, disproportionation products acid III and alcohol IV rather than aldehydes II are formed. The same substances are formed when the Cannizzarro reaction with aldehyde II is carried out

Krasnodar Polytechnic Institute, Krasnodar 350006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1168-1171, September, 1977. Original article submitted July 8, 1976; revision submitted January 31, 1977.

 0009-3122/77/1309-0938 $07.50

TABLE 1. 1,2-Di(2-furyl)ethylene Derivatives

Compound	R	R′	mp, °C	bp, °C (mm)	R_f[a]	M^+, found[b] (calc.)	Found, %		Empirical formula	Calc., %		UV spectrum (ethanol), λ_{max}, nm (log ε)	IR spectrum (mineral oil), cm^{-1}			Yield, %
							C	H		C	H		C=C	C=O	OH	
II[a]	H	CHO	58[c]		0,55	188 (188)	70,5	4,40	$C_{11}H_8O_3$	70,2	4,25	373 (4,19)	1630	1670		86—92
III[a]	H	COOH	168—169		0,30	204 (204)	64,9	3,70	$C_{11}H_8O_4$	64,5	3,90	340 (4,59), 362 (4,52)	1640	1695	1260, 1270	24
IV[a]	H	CH_2OH		180 (2) (dec.)	0,14	190 (190)	69,6	5,35	$C_{11}H_{10}O_3$	69,4	5,26	327 (4,20), 342 (4,19)	1630		3370	94
II[b]	CH_3	CHO	63[c]		0,50	202 (202)	71,0	5,15	$C_{12}H_{10}O_3$	71,2	4,95	382 (4,20)	1630	1670		94
III[b]	CH_3	COOH	160—161		0,26	218 (218)	65,9	5,00	$C_{12}H_{10}O_4$	66,0	4,60	348 (4,56), 369 (4,49)	1638	1685	1260, 1268	20
IV[b]	CH_3	CH_2OH		188 (2) (dec.)	0,10	204 (204)	71,0	5,95	$C_{12}H_{12}O_3$	70,6	5,88	332 (4,19), 347 (4,18)	1642		3370	96

[a]Thin-layer chromatography on Silufol in a chloroform—petroleum ether system (3 : 1).
[b]Mass spectrometrically.
[c]2,4-Dinitrophenylhydrazone.

in alcohol in the presence of KOH. In addition to the indicated substances, the reaction mixture contains certain amounts of pyromucic and 5-methylpyromucic acids and the corresponding furfuryl alcohols, the formation of which is due to Cannizzarro reaction of the starting furfurals, which, according to our observations, proceeds primarily in the case of catalysis by ethoxide at low temperatures.

A peculiarity and complexity of the synthesis is the constant linking of the condensation process with disproportionation of the starting aldehydes I or aldehydes II, as well as crossover processes.

Substances that do not decompose the ethoxide – various alcohols, benzene, dioxane, and ethyl ether – were checked as solvents. The reaction proceeds normally in practically all of these media, but it is better to obtain III and IV in dioxane and in ethanol, whereas II is obtained in good yield in benzene. This is apparently explained by the fact that dioxane and ethanol are better solvents for the water formed as a result of the reaction.

The two series of condensations – of 5-methylfurfural itself and of a mixture of 5-methylfurfural with furfural – require different approaches to the working out of the components of the mixture. The above-indicated amount of ethoxide was taken for the autocondensation of 5-methylfurfural, and the formation of only a small amount of 5-methylpyromucic acid and 5-methylfuryl alcohol should be expected in the reaction products. As we have seen, in the condensation of furfural with 5-methylfurfural a 1 : 1 ratio of the starting aldehydes is undesirable, since IIa, IIIa, IVa and IIb, IIIb, and IVb may be formed with equal probabilities in this case. In this connection, we adopted a more effective furfural to methylfurfural ratio of (2-3) : 1. A portion of the furfural in this case should remain unconsumed in the preparation of IIa, whereas a great deal of pyromucic acid and furfuryl alcohol accumulates in the mixture when excess catalyst is used for the preparation of IIIa and IVa. In view of the low yield of acid IIIa (up to 20-30%) and the considerable accumulation of pyromucic acid in the mixture, one may assume that a crossover Cannizzarro reaction between aldehyde IIa and furfural is likely. Alcohol IVa, which is formed in the high yield in this reaction, indicates that in the crossover reaction aldehyde IIa undergoes primary reduction, whereas furfural undergoes oxidation.

It should be noted that mixtures of furfural and methylfurfural (for example, "peat furfural") in a close ratio of 2 : 1, which can be used after dehydration for the preparation of IIa, IIIa, and IVa, are formed in a number of factories of the hydrolysis industry.

The separation of the reaction mixtures is complicated by two factors: the presence of furfural or furan alcohols and acids and by the fact that IIa,b and IVa,b are undistillable oils (at 2 mm the mixture undergoes resinification when it is heated above 100-150°C). Aldehyde IIa undergoes distillation with steam, but even in this operation the bulk of the material undergoes resinification in the distillation flask. Removal of the unchanged furfurals by washing out with water and subsequent precipitation by dilution of the dioxane solutions with water or of the benzene solutions with n-heptane give quite good results. In the latter case the benzene solution can be separated from the resinous substances, and alcohols IV can be precipitated by dilution with heptane. Aldehyde II remains in the heptane solution.

The structures of the compounds obtained were confirmed by the usual methods (Table 1) and also by identification with the spectral characteristics of polyene compounds. 1,2-Di(2-furyl)ethylene obtained by the method in [3] has a UV spectrum with two maxima at 323 and 340 nm. The spectra of II, III, and IV are shifted bathochromically in correspondence with the substituents of the furan rings. Thus 7-α-furyl-2,4,6-heptatrienal [6] (the polyene analog of IIa) absorbs at 366 and 382 nm (IIa absorbs at 373 nm). The spectra of structures close to those of IIb, IIIb, and IVb (retinol and its derivatives [7]) are also similar to the spectra of the compounds obtained (retinol at 325 nm and retinal at 375 nm).

The molecular weights of II-IV were confirmed by mass spectrometry.

EXPERIMENTAL

The UV spectra were obtained with a Specord UV-vis spectrophotometer. The IR spectra were obtained with a UR-20 spectrometer. The mass spectra were obtained with an MKh-1303 spectrometer; the temperature of the admission system was 250°C, the temperature of the ionization chamber was 250°C, and the ionizing-electron energy was 24 eV. The individuality of the substances was established with a Chrom-4 chromatograph; the adsorbent was Chezasorb, the stationary phase was 5% XE-60 (silicone rubber), and the column was programmed for 160-240°C.

1-(2-Furyl)-2-(2-formyl-5-furyl)ethylene (IIa). A) A total of 250 ml of a mixture of furfural and methylfurfural containing 35% (100 g or 0.9 mole) of the latter was added to a solution of 8 g (0.32 g-atom) of sodium metal in a mixture of 400 ml of absolute butanol and 300 ml of absolute benzene, and the mixture was then

thermostatted at 70° for 1 h with periodic selection of samples for spectral monitoring. The increase in the absorption at 350-400 nm and the decrease in the band of the mixture of furfurals at 270-300 nm indicate the formation and accumulation of IIa. At the end of the reaction the long-wave band remained stable vis-a-vis the simultaneous presence of the spectrum of excess furfural. The mixture was allowed to stand at room temperature overnight, after which it was poured into 2 liters of water containing 50 ml of concentrated HCl. The benzene layer was washed several times with water and dried with anhydrous Na_2SO_4, and the solvent was removed by vacuum distillation to give 145 g (86%) of a red oil.

B) A 2-g sample of sodium metal was dissolved in a mixture of 100 ml of absolute ethanol and 50 ml of absolute propyl alcohol, and 40 ml of a mixture of furfural and methylfurfural containing 20% of the latter was added without cooling. After spontaneous heat liberation ceased, the mixture was thermostatted on a bath for 1 h with moderate refluxing of the ether. It was then allowed to stand overnight, after which it was poured into 250 ml of water containing 10 ml of concentrated HCl. The reaction mixture was washed in a Drexel flask with a slow stream of water with the periodic addition of ether to maintain the reaction product in the upper layer. After we were convinced that furfural was no loger present in the wash waters (by spectral or hydrazine monitoring), the ether solution was dried and the ether was removed by distillation to give 12.5 g (92%) of a red oil.

1-(5-Methyl-2-furyl)-2-(2-formyl-5-furyl)ethylene (IIb). The synthesis was carried out in the manner described for IIa from 5-methylfurfural in a twofold quantity as against the amount introduced into the mixture with furfural.

1-(2-Furyl)-2-(2-hydroxymethyl-5-furyl)ethylene (IVa). A 9.3-g (0.05 mole) sample of aldehyde IIa was dissolved in 50 ml of alcohol, the solution was mixed with 50 ml of a concentrated aqueous solution of formaldehyde (an emulsion was formed), and 15 g of KOH in 40 ml of 50% alcohol was added. The decomposed mixture was cooled after 2 h and extracted with ether. The extract was washed several times with water and dried, and the ether was removed by distillation to give 8.9 g (95%) of a red oil.

1-(2-Furyl)-2-(2-hydroxymethyl-5-furyl)ethylene (IVa) and 1-(2-Furyl)-2-(2-carboxy-5-furyl)ethylene (IIIa). An alcohol solution of sodium ethoxide [from 15 g (0.65 g-atom) of sodium and 200 ml of alcohol] was added in the course of 1 h at 60°C to a mixture of 96 g (1 mole) of furfural, 55 g (0.5 mole) of 5-methylfurfural, and 100 ml of absolute alcohol. The reaction was exothermic, and the heating bath was therefore removed at the start of the addition of the ethoxide. The mixtures were allowed to cool, and 400 ml of ethanol was added to extract IVa. The resulting suspension of the salt of IIIa was removed by filtration, and the ether filtrate was washed with water and dried. The ether was removed to give 46 g (96%) of alcohol IVa.

The salt of IIIa was dissolved in 100 ml of water, the solution was filtered, and the filtrate was acidified to pH 3-4 with hydrochloric acid (the pyromucic acid impurity remained in solution). The precipitated IIIa was recrystallized from 50% alcohol to give 12 g (24%) of a product that was insoluble in water but quite soluble in organic solvents.

Compounds IIIb and IVb were obtained by a similar method from 5-methylfurfural. Data on these compounds are presented in Table 1.

We thank Professor V.G. Kul'nevich for his valuable instructions with respect to this research.

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