REACTIONS OF FURAN ALDEHYDES
4.* OXIDATION–REDUCTION REACTIONS OF FURFURAL WITH MONOHYDRIC ALCOHOLS

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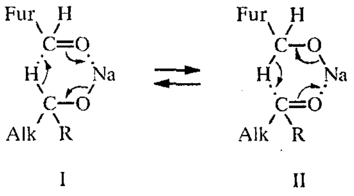
Furfural oxidizes aliphatic and alicyclic alcohols at 70-100°C under the action of sodium alcoholate to aldehydes and ketones, and then participates in a crotonate condensation. At 0-10°C the alcohol is not oxidized but the adduct with alkoxide ion is oxidized to form an alkyl furoate.

Unsaturated furan aldehydes and ketones were unexpectedly obtained in 30-70% yield when investigating the reactions of furfural in alcoholic media catalyzed by sodium alcoholate. This indicates that carbonyl compounds are formed in the mixture by oxidation of the solvent. These then undergo a crotonate condensation with unreacted furfural. Various unsaturated furan compounds from a wide range of homologous series may be obtained by this hitherto undescribed reaction without using difficultly available aldehydes and ketones.

The basis of this process is the oxidation–reduction reaction of furfural with an alcohol as in the Oppenauer, Meerwein–Ponndorf–Verley, and Tishchenko–Claisen reactions [2], where a decisive role is assigned to aluminum alcoholate as catalyst. Similar conversions are also observed in the Cannizzaro reaction [1, 3-5] where the aldehyde is reduced by the alcoholate of a gem-diol.

Evidently these conversions are linked by a single type of oxidation–reduction process, i.e., the transfer of hydride ion from the alcoholate of a mono- or dihydric alcohol to the carbonyl carbon.

The central step in the mechanism of these conversions seems to be the equilibrium between the transition states (I) and (II), the position of which depends on the ability of the reactant to lose hydrogen ion.



I, II R=H, Alk, OAlk, OH, O⁻ etc.

It was shown in [3, 5] that transfer of hydride ion is more probable the greater the electron-donating effect of the group R.

Results are given in the present work on an investigation of the conversions of furfural at various temperatures in a medium of a primary, secondary, or tertiary aliphatic or alicyclic alcohol in the presence of sodium alcoholate.

It was established that the formation of unsaturated compounds occurs at 70-100°C and esters accumulate at 0-10°C. Furfuryl alcohol is formed in significant quantities in the reaction mixture in each case.

The aliphatic aldehydes generated condense directly with unreacted furfural with the formation of furylacrolein or its β-homologs in 68-75% yield.

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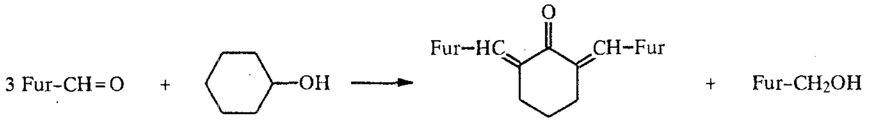
*For Communication 3, see [1].

Krasnodar Polytechnic Institute, Krasnodar 350670. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 25-28, January, 1993. Original article submitted September 10, 1991.

0009-3122/93/2901-0020$12.50

The corresponding difurfurylidene ketones are formed in 28-35% yield from secondary alcohols (the reaction was investigated in a medium of 2-propanol and cyclohexanol), for example:



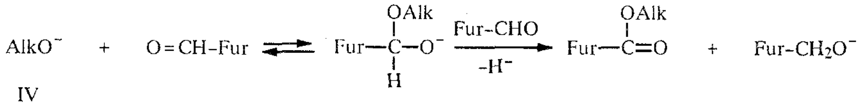
[6 In t-butyl alcohol solution only the disproportionation products of furfural were obtained, which confirms the decisive role of hydride transfer in this reaction.

It was also established that β-homologs of furylacrolein are formed in aqueous alcoholic solutions of furfural containing NaOH and NaBr and by electrolysis on graphite electrodes. The generation of Br_2 at the anode in the alkaline medium leads to the formation in the electrolytic cell of hypobromite and oxidation of the alcohol to ketone and its subsequent crotonate condensation. This case, seemingly of no practical interest in view of the duration of the process and the low recovery of the product, is convenient for confirming the oxidation–reduction mechanism of the synthesis.

Boiling an alcoholic solution of an unsaturated aldehyde or ketone with an excess of alcoholate leads to the formation of an unsaturated alcohol containing a furan group in 38-42% yield [6, 7] as the product of a second oxidation–reduction process.

$$\text{Fur-CH=CR-CH=O} + \text{RCH}_2\text{-CH}_2\text{-O}^- \rightarrow \text{Fur-CH=CR-CH}_2\text{O}^- + \text{RCH}_2\text{-CH=O}$$

The process is different at 0-10°C. No unsaturated compounds were detected among the reaction products, only furoic acid esters in 48-55% yield [8]. As is seen, by analogy with the Tishchenko reaction [5], nucleophilic addition of alkoxide anion to the carbonyl carbon is here observed with subsequent consumption of hydride ion in the reduction of a furfural molecule to furfuryl alcohol.



$$\underset{\text{IV}}{\text{AlkO}^-} + \text{O=CH-Fur} \rightleftharpoons \underset{\text{III}}{\text{Fur—}\overset{\text{OAlk}}{\underset{\text{H}}{\text{C}}}\text{—O}^-} \xrightarrow[\text{-H}^-]{\text{Fur-CHO}} \text{Fur—}\overset{\text{OAlk}}{\text{C}}\text{=O} + \text{Fur-CH}_2\text{O}^-$$

IV

III

The furfural adduct (III) is more active than the alcoholate (IV) as a donor of hydride ion in the complex (I), consequently of the two possible reactions esters are formed at reduced temperature. On increasing the temperature the unstable adduct (III) decomposes to the starting materials which also leads to the formation of unsaturated compounds.

Preliminary investigations with benzaldehyde showed a similarity to the reactions of furfural. Thus, the corresponding homolog of cinnamaldehyde is obtained in a medium of propyl alcohol.

EXPERIMENTAL

The identification and investigation of the properties of the compounds obtained were performed by UV and IR spectroscopy (on Specord UV-VIS and Specord IR instruments), mass spectrometry (MX 1303 instrument, temperature of the inlet system and ionization chamber 250°C, energy of ionizing electrons 24 eV), and by elemental analysis.

Examples of syntheses are given below.

α-Methyl-β-(2-furyl)acrolein [(VIb), $C_8H_8O_2$]. Sodium (4.6 g: 0.2 mole) was dissolved in propyl alcohol (300 ml) at 60°C in a 1-liter three-necked flask fitted with a stirrer passing through the reflux condenser. The temperature of the sand bath was increased to the boiling point (97°C) and freshly distilled furfural (48 g: 0.5 mole) was added dropwise with vigorous stirring during 1 h, after which the mixture was boiled for 1 h. The cooled reaction mixture was poured into diethyl ether (800 ml) and the precipitate of alcoholate filtered off. The ether layer was washed with water, dried, and distilled. The product (23.1 g: 68%) was taken at bp 99-101°C (12 mm). M^+ 136. IR spectrum: 1620 (C=O), 1400-1600 (C=C ring), 1020 (C–O–C) cm^{-1}. λ_{max} 320 nm, log ε 4.21 in ethanol (analogous data in [9]).

Difurfurylidenecyclohexanone ($C_{16}H_{14}O_3$). The synthesis was carried out similarly to that described above but using cyclohexanol as solvent. The product was obtained in 28.2% yield, bp 142.5°C. M^+ 254. λ_{max} 382 nm, log ε 4.7. Boiling this ketone after adding additional portions of alcoholate gave difurfurylidenecyclohexanol.

TABLE 1. Characteristics of Synthetic Products

Solvent	Compounds V—VII				
	Fur—COOR		Fur—CH=C—CRR^1		
	V		VI R^1=CH=O		VII R^1=CH_2OH
	R	bp, °C (mm)	R	bp, °C (mm)	
Ethanol	C_2H_5	90(12)	H	51*	112(12)
Propanol	C_3H_7	112(14)	CH_3	100(12)	140(12)
Butanol	C_4H_9	107(10)	C_2H_5	119(12)	166(12)
t-Butanol	C_4H_9	117(7)	—	—	—
Pentanol	C_5H_{11}	125(5)	C_3H_7	126(12)	177(10)

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*mp.

β-Methyl-γ-(2-furyl)allyl alcohol [(VIIb), $C_8H_{10}O_2$]. Metallic sodium (4.6 g: 0.2 mole) was dissolved in propyl alcohol (300 ml) in a 1-liter round-bottomed flask fitted with a stirrer passing through the reflux condenser. Using the sand bath the temperature was increased until the solvent boiled and freshly distilled furfural (48 g: 0.5 mole) was added during 1 h with vigorous stirring. Then propyl alcohol (30 ml) in which sodium (2.3 g: 0.1 mole) was dissolved was poured in. The mixture was boiled for 5 h, cooled, and poured into diethyl ether (600 ml). The solid was filtered off and the solution distilled. The product was collected as a yellow oil at 140-142°C (12 mm). M^+ 138. IR spectrum: 3360 (OH), 1620 (C=C branch) cm^{-1}. λ_{max} 265, 275 nm, log ε 4.20, 4.06 in ethanol (corresponding to the data of [9]). Yield 12.5 g (36.4%).

Pyromucic Acid Amyl Ester [(Vd), $C_{10}H_{14}O_3$]. Sodium (11.5 g: 0.5 mole) was dissolved in absolute amyl alcohol (500 ml), the solution cooled to 5°C, and freshly distilled furfural (96 g: 1 mole) poured in during 1.5 h, keeping the temperature in the flask below 10°C. The mixture was kept at 0-5°C for 15 h, then poured into diethyl ether (2 liter), and the precipitated solid filtered off. The filtrate was washed with water, dried over sodium sulfate, and distilled. The product was taken as a yellow oil at 125°C (5 mm). A second distillation gave 66 g product (54.5% on the furfural reacted). M^+ 182. IR spectrum: 1720 (C=O), 1530 (C=C), 1010 (C—O—C) cm^{-1}. λ_{max} 255 nm, log ε 4.12 in ethanol (analogous data were given in [9]).

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