UDC 542.941.7 + 547.723

RESEARCHES ON FURAN COMPOUNDS

XXXI. Hydrogenation of Furans with Oxygen Functional Groups Over Ruthenium Catalysts*

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 2, pp. 163–168, 1966

This paper gives the results obtained by liquid phase catalytic hydrogenation under pressure, over ruthenium catalysts, of furan aldehydes, ketones, and carboxylic acids. It is shown that the ruthenium catalysts are highly effective for hydrogenating the furan ring, ethylenic double bonds, and the carbonyl group, though they are not selective with respect to them. At room temperature the furan ring is mostly reduced to a tetrahydrofuran one. It is confirmed that compounds containing the 1, 6-dioxaspiro [4, 4]-nonane grouping are formed by hydrogenating furfurylidene aldehydes and ketones, and γ-furylalkanols.

The catalysts usually used for hydrogenating furan compounds are Raney nickel, copper chromite, platinum (Adams), palladium on active charcoal, and some others.

The order of hydrogenation of different bonds in furan compounds over ruthenium has been investigated in detail, and a theoretical interpretation given, based on the multiplet theory [1, 2].

A series of reviews [3–5] gives exhaustive data regarding hydrogenation of furan derivatives over various catalysts, but results on hydrogenation over ruthenium compounds are almost completely absent from the literature. Howk [6] successfully used a ruthenium catalyst for hydrogenating furfural. Furfuryl alcohol was obtained by hydrogenating under mild conditions over 5% Ru/Al_2O_3 [7]. It is also known [8] that the furan ring in furan amines is hydrogenated over ruthenium catalysts.

Our previously begun systematic studies [9–13] of the catalytic properties of ruthenium for liquid phase hydrogenation revealed its high activity. The present paper gives the experimental results obtained in liquid phase hydrogenation of some furan compounds (alcohols, aldehydes, ketones, and acids) containing oxygen functional groups. The catalysts were ruthenium dioxide and ruthenium on charcoal (5% Ru/C). The present authors previously developed methods for making these catalysts [13, 14].

Table 1

Hydrogenation of Furan Alcohols

Starting compound*	Catalyst	Run temperature, °C	Reaction product **	Yield, %
$F-CH_2OH$	Ru/C	20	$THF-CH_2OH$	90.1
	RuO_2	20	”	95.3
$F-(CH_2)_3-OH$	Ru/C	20	1) $THF-(CH_2)_3-OH$ 2) 1,6-Dioxaspiro [4,4]nonane***	83.1 12.8
	RuO_2	15	$THF-(CH_2)_3-OH$	93.7
$F-(CH_2)_2-\underset{OH}{\underset{\vert}{CH}}-CH_3$	Ru/C	21	1) $THF-(CH_2)_2-\underset{OH}{\underset{\vert}{CH}}-CH_3$ 2) 2-Methyl-1, 6-dioxaspiro [4,4]nonane	78.1 14.6
	RuO_2	19	$THF-(CH_2)_2-\underset{OH}{\underset{\vert}{CH}}-CH_3$	93.8

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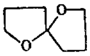
*Here and subsequently F is α-furyl.

** Here and subsequently THF is α-tetrahydrofuryl.

***Formula of the compound 

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*For Part XXX see [15].

Furan alcohols are hydrogenated under quite mild conditions over ruthenium catalysts to the corresponding tetrahydrofuran alcohols. Table 1 gives the experimental results. It should be mentioned that when the 5% Ru/C catalyst is used for hydrogenating 1-(α-furyl) propan-3-ol and 1-(α-furyl) butan-3-ol, considerable amounts of the corresponding spirans with the 1, 6 dioxaspiro [4, 4]-nonane group are formed.

Investigation of the hydrogenation of furan aldehydes and ketones is of both theoretical and practical interest. The hydrogenation of furfural is of special interest in this connection. Hydrogenation of furan aldehydes and ketones can give rise to various products, e.g., hydrogenation of furylacrolein can proceed thus:

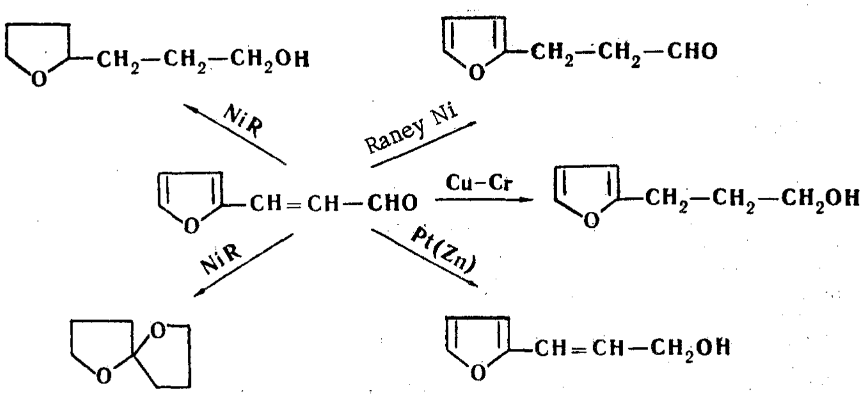

Table 2 shows that furan aldehydes and ketones generally hydrogenate under mild conditions over ruthenium, the former being reduced with greater difficulty than the latter. For example, if furfural or 1-(α furyl) acrolein is hydrogenated at room temperature to the corresponding furan alcohol only, furfurylideneacetone or 1-(α-furyl) butan-3-one is converted under the same conditions to tetrahydrofuran alcohol and 2-methyldioxaspiro [4, 4] nonane respectively (Table 2).

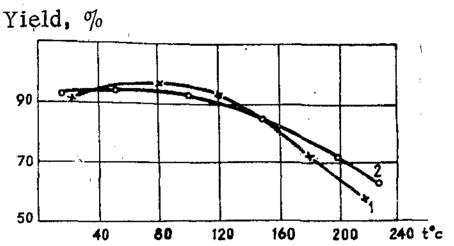

Fig. 1. Yield of tetrahydrofurylbutan-3-ol as a function of temperature: 1) Over Ru/C; 2) over RuO_2.

Investigation of the effect of temperature on hydrogenation of furan aldehydes and ketones shows that optimum yields of tetrahydrofuran alcohols are obtained at 80°. Raising the temperature to above 150° results in rapid lowering of the yields of tetrahydrofuran alcohols, due to accompanying hydrogenolysis (Fig. 1).

Hydrogenation of furan aldehydes and ketones over 5% Ru/C catalyst gives a considerable amount of 1, 6-dioxaspiro [4, 4]-nonane group spirans. It is of interest that increase in time of catalyst service leads to gradual change of selectivity with respect to formation of tetrahydrofuran alcohol and spiran (Fig. 2).

The results in Table 2 show that a ruthenium catalyst is practically unselective, and simultaneously hydrogenates different multiple bonds in aldehyde and ketone molecules, as the hydrogenation products do not contain unsaturated linkages.

With the catalysts used, hydrogenation of furan aldehydes, ketones, and alcohols proceeds only under pressure. Investigation of the effect of pressure on hydrogenation of these compounds shows that over 40 atm the reaction is of zero order for hydrogen, and that below 20 atm hydrogenation practically ceases.

Over ruthenium catalysts, pyromucic and furylacrylic acids hydrogenate under quite mild conditions (Table 3). It is of interest that hydrogenation of furan acids in an alcohol at high temperatures leads to one-step formation of esters derived from the alcohol and tetrahydrofuran acid.

Experimental

Preparing the ruthenium catalysts [13, 14]. Ru metal was the starting material for making the catalysts. To prepare RuO_2, potassium ruthenate, obtained by alkali fusion of Ru in the presence of an oxidizing agent, was converted to the hydroxide of Ru^{IV}, and the latter at high temperatures gave the dioxide. To prepare the 5% Ru/C catalyst, the Ru^{IV} hydroxide prepared from the ruthenate was converted to hydroxychloride, and the latter applied to the active charcoal from $EtOH-H_2O$ solution.

The catalysts were reduced at 100° in an autoclave, the medium being the compound to be hydrogenated, or acetone.

Table 2

Hydrogenation of Furan Aldehydes and Ketones*

Starting compound	Catalyst	Run temperature, °C	Reaction product	Yield, %
$F-CHO$	Ru/C	20	$F-CH_2OH$	71.2
	RuO_2	80	$THF-CH_2OH$	89.3
$F-CH{=}CH-CHO$	Ru/C	20	$F-(CH_2)_3-OH$	78.3
	RuO_2	80	1) $THF-(CH_2)_3-OH$ 2) 1,6-Dioxaspiro [4,4]nonane	68.3 12.2
	Ru/C	100	$THF-(CH_2)_3-OH$	84.1
$F-(CH_2)_2-\underset{\overset{\vert}{CH_3}}{C}{=}O$	Ru/C	20	1) $THF-(CH_2)_2-\underset{\overset{\vert}{CH_3}}{CH}(OH)$ 2) 2-Methyl-1,6-dioxaspiro-[4,4]-nonane	77.4 18.4
$F-CH{=}CH-\underset{\overset{\vert}{CH_3}}{CO}$	Ru/C	20	1) $THF-(CH_2)_2-\underset{\overset{\vert}{CH_3}}{CH}(OH)$ 2) 2-Methyl-1,6-dioxaspiro [4,4]-nonane	75.1 15.3
	RuO_2	20	$THF-(CH_2)_2-CH(OH)-CH_3$	92.1
2-Monofurfurylidene-cyclohexanone**	Ru/C	19	1) 1-(α-Tetrahydrofurfuryl) cyclohexan-2-ol 2) Spiro (perhydrobenzofuran-2,2'-tetrahydrofuran)***	76.5 15.3
$F-CH{=}CH-\underset{\overset{\Vert}{O}}{C}-C_6H_5$	RuO_2	120	$THF-(CH_2)_2-\underset{\overset{\vert}{OH}}{CH}-C_6H_{11}$	79.9
$F-CH{=}CH-CH{=}CH-\underset{\overset{\Vert}{O}}{C}-CH_3$	RuO_2	80	$THF-(CH_2)_4-CH(OH)-CH_3$	73

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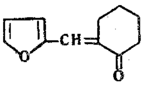
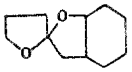
*See footnote to Table 1.

** Structure of compound 

*** Structure of compound 

Hydrogenation procedure. The solution (solvents used were MeOH, EtOH, H_2O) of the compound to be hydrogenated was placed in the autoclave, followed by the catalyst, and then the hydrogen admitted. Temperature regulation was with a type EPVI-11A automatic electronic potentiometer, and hydrogen uptake was checked with a MKD type manometer. When hydrogen absorption was ended, the autoclave was emptied, the catalyst filtered off, the solvent distilled off under reduced pressure, and the residue vacuum-distilled.

Reaction products were identified by their boiling points and refractive indices, while in some cases use was made of the IR and UV spectra too.

Below are given briefly data relating to the properties and analyses of the first compounds obtained.

1-(α-Tetrahydrofurfuryl) cyclohexan-2-ol. Oily liquid which did not darken on storage, 111.5-113° (2 mm), n_D^{20} 1.4905, d_4^{20} 1.0372. Found: C 71.24, 71.45; H 10.83, 10.82; OH 8.92, 8.88%; M 183.20, 184.20; MR_D 51.31. Calculated for $C_{11}H_{20}O_2$, C 71.68; H 10.94; OH 9.20%; M 184.28; MR_D 51.77. IR spectrum data show that there is no furan ring present.

Spiro (perhydrobenzofuran-2, 2-tetrahydrofuran). Oily liquid with a marked, pleasant odor, bp 89-91° (3 mm); n_D^{20} 1.4828; d_4^{20} 1.0431. Found: C 72.12, 72.19; H 10.66, 10.40%. M 181.50, 180.90. No hydroxyl (Terent'ev)

MR_D 49.59. Calculated for $C_{11}H_{18}O_2$: C 72.47; H 9.95%; M 182.26; MR_D 49.60. This compound was previously prepared by another method, by one of the present authors and I. A. Markushina [18].

Table 3

Hydrogenation of Furan Acids*

Starting compound	Catalyst	Run temperature, °C	Solvent	Reaction product	Yield, %
F — COOH	Ru/C	100	H_2O	THF — COOH	43.5
	RuO_2	20	H_2O		57.0
	RuO_2	100	H_2O		64.0
	RuO_2	100	CH_3OH	1) THF — COOH	48.3
				2) THF — $COOCH_3$	39.1
	RuO_2	100	C_2H_5OH	1) THF — COOH	40.0
				2) THF — $COOC_2H_5$	45.0
F — CH=CH—COOH	Ru/C	100	H_2O	THF — CH_2—CH_2—COOH	68.5
	RuO_2	80	H_2O		51.2
	RuO_2	20	CH_3OH		84.0
	RuO_2	100	CH_3OH	1) THF — CH_2—CH_2—COOH	74.1
				2) THF — CH_2—CH_2—$COOCH_3$	18.8

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*See note in Table 1.

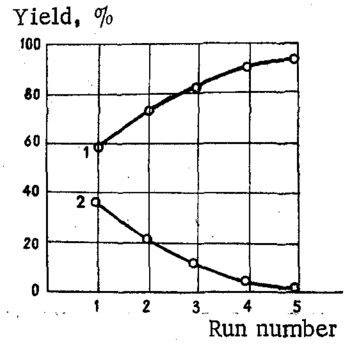

Fig. 2. Yields of 1-(α-tetrahydrofuryl)butan-2-ol and 2-methyl-1, 6-dioxaspiro [4, 4]-nonane as a function of catalyst service time in the hydrogenation of furfylideneacetone over Ru/C: 1) spiran yield; 2) alcohol yield.

1-Cyclohexyl-3-(α-tetrahydrofuryl) propan-1-ol. Almost odorless liquid, bp 155–157° (5 mm); n_D^{20} 1.4868; d_4^{20} 1.0020. Found: C 73.15, 73.59; H 11.68, 11.51; OH 8.19, 7.87%; M 212.5, 211.9; MR_D 60.89. Calculated for $C_{13}H_{24}O_2$: C 73.55; H 11.39; OH 8.02%; M 212.3; MR_D 61.00.

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7 December 1964

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