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LIQUID-PHASE HYDROFORMYLATION OF 2,3- AND 2,5-DIHYDROFURANS

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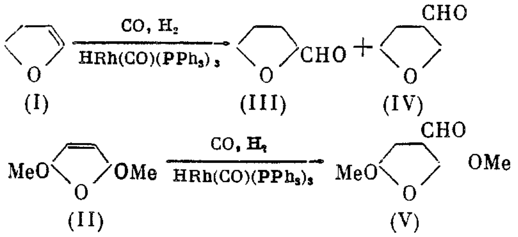
The synthesis of 3-formyl derivatives of the tetrahydrofuran series was carried out by hydroformylation of 2,3-dihydrofuran and 2,5-dimethoxy-2,5-dihydrofuran in the presence of $HRh(CO)(PPh_3)_3$. The influence of the temperature, pressure, catalyst concentration, and the nature of the solvent on the conversion of dihydrofuran, the composition of aldehydes obtained and the selectivity of their formation was investigated.

Aldehydes of the tetrahydrofuran series are valuable intermediates for the synthesis of heterocyclic compounds, in several cases having biological activity [1-4].

The aim of the present work was to synthesize formyl derivatives of the tetrahydrofuran series by hydroformylation of 2,3- and 2,5-dihydrofurans in the presence of $HRh(CO)(PPh_3)_3$. The hydroformylation was carried out under pressure in the liquid phase.

We studied the influence of temperature, pressure, the catalyst concentration, and the nature of the solvent on the hydroformylation of 2,3-dihydrofuran (I) and 2,5-dimethoxy-2,5-dihydrofuran (II)



In the study of the influence of temperature, pressure, and duration of the hydroformylation of (I), the solvent used was benzene (Table 1). It was found that with increase in the temperature, pressure and duration of the experiments, the conversion of (I) increases, while the selectivity of the formation of the aldehydes (Fig. 1) and the 2-formyltetrahydrofuran/3-formyltetrahydrofuran (III)/(IV) ratio in the reaction products decreases. The greatest increase in the content of (IV) in the reaction products with increase in the duration of the experiment is observed at a pressure of 140 atm.

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TABLE 1. Influence of Temperature, Pressure, Duration of Reaction (τ) on the Hydroformylation Process of 2,3-Dihydrofuran in Benzene $[(I)]/[HRh(CO)(PPh_3)_3] = 300$

P, atm	T, °C	τ, min	Conversion of (I), %	(III)/(IV)
60	60	30	31	1.3
	60	90	85	1.1
	90	30	85	1.1
	90	90	100	1.1
	130	30	100	1.8
	130	90	100	1.3
100	60	30	54	1.6
	60	90	92	1.2
	90	30	77	1.6
	90	90	100	1.2
	130	30	100	1.3
	130	90	100	1.2
140	60	30	62	1.9
	60	90	69	1.6
	90	30	92	2.3
	90	90	96	1.3
	130	30	100	1.9
	130	90	100	1.1

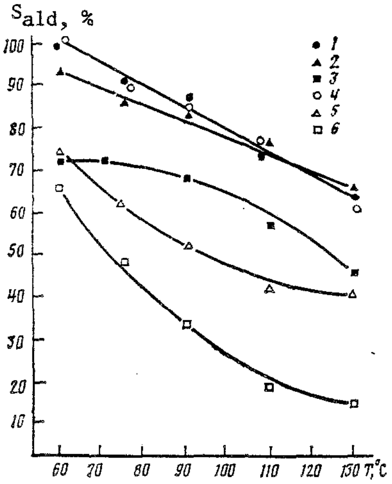

Fig. 1

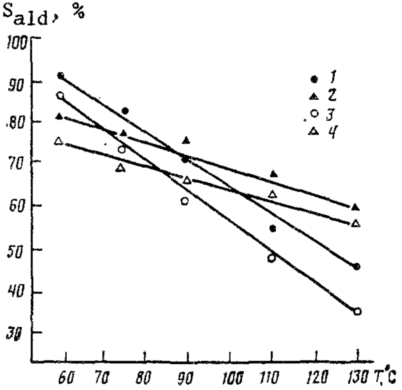

Fig. 2

Fig. 1. Dependence of overall selectivity of formation of aldehydes (III) and (IV) in the hydroformylation of 2,3-dihydrofuran on temperature: 1) 30 min, 60 atm; 2) 30 min, 100 atm; 3) 30 min, 140 atm; 4) 90 min, 60 atm; 5) 90 min, 100 atm; 6) 90 min, 140 atm.

TABLE 2. Influence of Temperature and Catalyst Concentration on Hydroformylation of 2,3-Dihydrofuran in Et_3N (P = 100 atm; $CO/H_2 = 1/1$; $[(I)]/[HRH(CO)(PPh_3)_3] = 300$; τ = 90 min)

T, °C	Conversion of (I), %	Selectivity of formation of (III) and (IV), %	(IV)/(III)	Selectivity of formation of THFA,* %
60	50	52	1.5	11
60 **	45	43	1.2	7
90	96	51	4.0	11
90 **	92	23	3.0	8
130	100	27	5.0	13
130 **	92	15	3.0	11

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*THFA — tetrahydrofuryl alcohol.

**$[(I)]/[HRh(CO)(PPh_3)_3] = 1300$ (molar).

The study of the influence of the nature of the solvent on the hydroformylation process of (I) showed that the overall yield of aldehydes (III) and (IV) is highest in less polar solvents, but the selectivity of the hydroformylation with respect to (IV) is low. The maximum content of (IV) in the reaction products was observed during the hydroformylation of (I) in NEt_3. To increase the yield of (IV) during the hydroformylation of (I) in NEt_3, we varied the reaction temperature and the concentration of the catalyst (Table 2). We found that with

TABLE 3. Influence of Temperature, Pressure and Duration of Reaction on Hydroformylation of (II) in Benzene [(II)]/[$HRh(CO)(PPh_3)_3$] = 300

P, atm	T, °C	τ, min	Conversion of (II), %	P, atm	T, °C	τ, min	Conversion of (II), %
60	60	30	59	100	60	30	93
	60	90	80		60	90	100
	90	30	90		90	30	100
	90	90	89		90	90	100
	130	30	90		130	30	100
	130	90	91		130	90	100

increase in the temperature, the conversion of (I) and the (IV)/(III) ratio increase, while the overall selectivity of formation of the aldehydes decreases. Decrease in the concentration of the catalyst lowers the conversion of (I), the overall selectivity and the (IV)/(III) ratio.

It was found that the influence of temperature, pressure, and duration of the reaction on the hydroformylation of (II) is similar to the influence of the same parameter during the hydroformylation of (I) (Table 3, Fig. 2).

EXPERIMENTAL

The hydroformylation was carried out in a Kh18N10T rotary stainless steel autoclave (0.15 liter). A 0.043 mmole portion (0.0344 g) of $HRh(CO)(PPh_3)_3$ [5], 5 ml of the solvent and 0.013 mole of (I) or (II) were charged into the autoclave. The autoclave was filled with a mixture of CO and H_2 ($CO/H_2 = 1/1$) to the required pressure, and was placed in an electrically heated furnace.

The reaction products were analyzed on a LKhM-8MD chromatograph with a catharometer-detector (a 2.5 m × 3 mm column with 5% of SE-30 silicone on N-AW chromaton; flow rate of carrier gas 20-30 ml/min, 50-120°C).

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