REACTIVITIES OF SOME CARBONYL COMPOUNDS OF THE FURAN SERIES IN CATALYTIC HYDROGENATION

R. Mat'yakubov, E. G. Abduganiev,
and V. S. Kozhevnikov

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The rate of hydrogenation of some carbonyl compounds of the furan series on Raney nickel—titanium—aluminum and copper—chromium oxide catalysts decreased in proportion to the decrease in the frequency of the absorption band of the C=O bond.

The available literature data [1, 2] do not make it possible to quantitatively characterize the dependence of the reactivity on the structure of furan compounds, except for a study [3] in which it is shown that there is a linear relationship between the K bands of the absorption spectra (when the solvent is replaced) and the logarithms of the rate constants for catalytic acetylation of some furan aldehydes. In the present research we studied the dependence of the reactivities of various ketones of the furan aseries on their structure in liquid-phase hydrogenation on copper—chromium oxide and Raney nickel—titanium—aluminum catalysts (Tables 1 and 2). It is known [4] that the frequencies of the absorption band of the carbonyl band can be selected as a measure of the polar effects.

TABLE 1. Rate of Hydrogenation* of Various Ketones on a Raney Nickel—Titanium—Aluminum Catalyst (hydrogen pressure 60 atm)

Compound undergoing hydrogenation†	Reaction rate $\cdot 10^{-3}$ mole/min at						
	20°C	35°C	60°C	70°C	100°C	120°C	140°C
Difurfurylideneacetone (I)	0,60	1,10	3,60	3,90	7,01	7,10	7,20
1,5-Difurylpent-1-en-3-one (II)	—	—	—	4,0	7,63	7,71	—
1,5-Difurylpentan-3-one (III)	0,12	0,19	0,35	0,39	0,44	0,49	0,60
1,5-Ditetrahydrofurylpentan-3-one (IV)	0,09	0,16	0,29	0,31	0,35	0,41	0,48

*Conditions: 250 ml of 2-propanol, 1.5 g of the catalyst, and 0.07 mole of the ketone.
†See Table 3 for νCO.

TABLE 2. Rate of Hydrogenation* of Various Unsaturated Ketones on a Raney Nickel—Titanium—Aluminum Catalyst (atmospheric pressure)

Compound undergoing hydrogenation†	Reaction rate $\cdot 10^{-3}$ mole/min at			
	20°C	35°C	50°C	65°C
Difurfurylideneacetone (I)	0,51	0,72	0,89	0,96
1,5-Difurylpent-1-en-3-one (II)	0,35	0,60	0,81	0,88
1-(α-Furyl)-5-phenylpenta-1,4-dien-3-one (V)	0,32	0,41	0,47	0,52
1,5-Di(α-furyl)-2-methylpenta-1,4-dien-3-one (VI)	0,13	0,16	0,19	0,22

*Conditions: 30 ml of 2-propanol, 0.40 g of the catalyst, and 0.01 mole of the ketone.
†For V, νCO 1660 cm^{-1}; for VI, νCO 1675 cm^{-1}.

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TABLE 3. Dependence of the Rate of Hydrogenation* of Various Ketones on a Copper—Chromium Oxide Catalyst on Their Structures (hydrogen pressure 60 atm)

Compound undergoing hydrogenation	νCO, cm^{-1}	Reaction rate $\cdot 10^{-3}$ mole/min
Difurfurylideneacetone (I)	1620	12,0
1,5-Di(α-furyl)pent-1-en-3-one (II)	1645	11,6
Furfurylideneacetone (VII)	1685	12,6
1-(α-Furyl)butan-3-one (VIII)	1726	5,1
1-(α-Tetrahydrofuryl)butan-3-one (IX)	1730	4,6
1,5-Di(α-furyl)pentan-3-one (III)	1725	0
1,5-Di(α-tetrahydrofuryl)pentan-3-one (IV)	1746	0

*Conditions: 250 ml of propanol, 1.5 g of the catalyst, 15 g of the ketone, and reaction temperature 130°C.

We have established that the rates of hydrogenation of the investigated ketones decrease in proportion to the decrease in the frequency of the absorption band of the C=O bond in the IR spectrum (see Table 3) over the entire investigated temperature range and that the rates of hydrogenation of all of the α,β-unsaturated ketones increase linearly as the temperature is raised.

It is known [5] that conjugated double bonds are usually more reactive in catalytic hydrogenation reactions than their unconjugated analogs. Difurfurylideneacetone therefore underwent hydrogenation at the highest rate in the investigated series.

The fact that 1,5-di(α-furyl)-2-methylpenta-1,4-dienone is reduced at the lowest rate is explained by a decrease in the reactivity and adsorbability of the molecule. As shown in [6], alkyl groups in the α position of α,β-unsaturated ketones decrease the reactivity and adsorbability of ethylene bonds significantly.

A comparison of the rates of hydrogenation of various ketones on the copper—chromium oxide catalyst under a hydrogen pressure of 60 atm with the frequencies of the absorption bands of the carbonyl bond in the IR spectra showed that their rates of hydrogenation decrease in proportion to the decrease in the frequency of the absorption band of the C=O bond. The higher rate of hydrogenation in the furfurylidenacetone molecule is evidently explained by keto-enol tautomerism; the enol form is probably hydrogenated much faster than the keto form. The close rates of hydrogenation of ketones II and VII constitute evidence for this.

Thus in the hydrogenation of furan ketones the reaction rates on both the Raney nickel—titanium—aluminum and copper—chromium oxide catalysts change as the structure becomes more complex: The rates of hydrogenation decrease proportionately with the decrease in the frequencies of the absorption bands of the carbonyl group.

EXPERIMENTAL

The copper—chromium oxide catalyst was reduced immediately prior to the experiments at 230°C in a stream of hydrogen for 2 h. The preparation of the nickel—titanium catalyst and the hydrogenation were carried out by previously described methods [7, 8].

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POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES.

1. SYNTHESIS OF TRI- AND TETRAFURYLMETHANES

V. G. Kul'nevich, S. V. Zhuravlev,
and L. A. Solonenko

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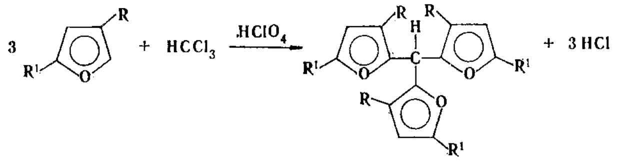
Derivatives of tri- and tetrafurylmethane were obtained by the reaction of alkylfurans with chloroform and carbon tetrachloride in benzene in the presence of catalytic amounts of 58% $HClO_4$.

Compounds of the furan series are widely used in industry, agriculture, and medicine, and the development of methods for the synthesis of compounds that contain several furan rings is therefore an important trend in the chemistry of heterocycles. Little study has been developed to tri- and tetrafurylalkanes, and methods for their synthesis have not been developed.

It is known that a substituted trifurylmethyl chloride is formed in the reaction of carbon tetrachloride with methyl pyromucate [1]. The preparation of polyfurylmethanes by alkylation of furan derivatives with donor substituents by means of chloroform and carbon tetrachloride has not been described. This is understandable, since the furan ring is readily destroyed by the action of protic and aprotic acids [2].

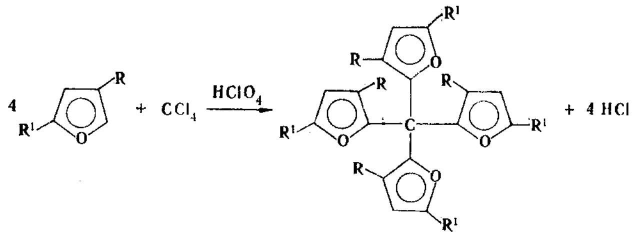
We have established that the reaction of alkylfurans with chloroform in benzene in the presence of catalytic amounts of 58% $HClO_4$ leads to the formation of trifurylmethanes in 75-87% yields.



I–V

I—IV R=H; I $R^1=CH_3$; II $R^1=C_4H_9$; III $R^1=C_5H_{11}$; IV $R^1=C_7H_{15}$; V $R=CH_3$, $R^1=C_7H_{15}$

The reaction of alkylfurans with CCl_4 under similar conditions makes it possible to obtain tetrafurylmethane derivatives in 78-87% yields.



VI–IX

R=H; VI $R^1=C_4H_9$; VII $R^1=C_5H_{11}$; VIII $R^1=C_7H_{15}$; IX $R=CH_3$, $R^1=C_7H_{15}$

Krasnodar Polytechnic Institute, Krasnodar 350006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 450-453, April, 1983. Original article submitted March 25, 1982.