HYDROGENATION OF DIFURFURYLIDENEACETONE ON A RANEY NICKEL CATALYST

R. Mat'yakubov, Yu. M. Mamatov,
N. Kh. Mukhamadaliev, and E. G. Abduganiev

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1.5-Difurylpent-1-en-3-one, 1,5-difurylpentan-3-one, 1,5-ditetrahydrofurylpentan-3-one, and 1,5-ditetrahydrofuryl-pentan-3-ol were obtained by hydrogenation of difurfuryldieneacetone on a Raney nickel catalyst at 20-65°C and atmospheric pressure. It was established that the hydrogenation of difurfuryldieneacetone is a zero-order reaction with respect to the concentration of the starting compound. The rate constants of the reaction were found; the activation energy found for 20-65°C is 6.2 ± 0.5 kcal/mole.

The literature contains sufficient data on the catalytic hydrogenation of difurfuryldieneacetone (I) in the presence of oxide catalysts. The use of a copper–chromite catalyst leads to the formation of 1,5-difurylpentan-3-ol as the principal reaction product [1]; 1,5-ditetrahydrofurylpentan-3-ol was obtained by hydrogenation on a nickel oxide catalyst [2]. Little study has been devoted to hydrogenation on a Raney nickel catalyst. 1,5-Difurylpentan-3-one was obtained when a nickel catalyst inhibited by chloroform and methyl iodide was used [3-4]. The role and effect of sodium hydroxide on the direction of the hydrogenation over a nickel catalyst were demonstrated in [5]. The reaction products in this case are 1,5-difurylpentan-3-one when sodium hydroxide is absent and 1,5-difurylpentane when it is present.

We have investigated the stepwise character of the catalytic hydrogenation of ketone I on a Raney nickel catalyst. The spin–spin coupling constant (SSCC) of the 1 and 2 vinyl protons in the PMR spectrum of I, which was used in the present research, is 15.0 Hz (Table 1), which indicates its trans,trans configuration. The studies were conducted in the kinetic region. We described the occurrence of the reaction in the kinetic region in [6]. The kinetic curves of the hydrogenation of ketone I in propanol at atmospheric pressure and 50°C are presented in Fig. 1. It is apparent from Fig. 1 that the start of the appearance of 1,5-difurylpent-1-en-3-one (II) coincides with the start of the entry of I into the reaction.

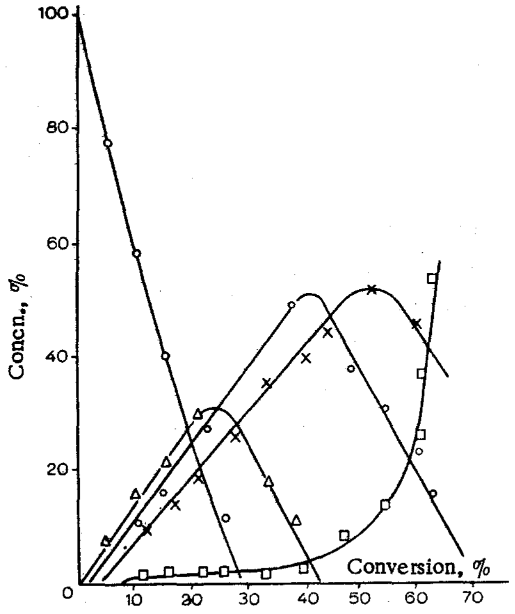

Fig. 1. Kinetic curves of the consumption and accumulation of the products of hydrogenation at 50°C of 2.14 g of dienone I with 0.40 g of the catalyst in 30 ml of propanol.

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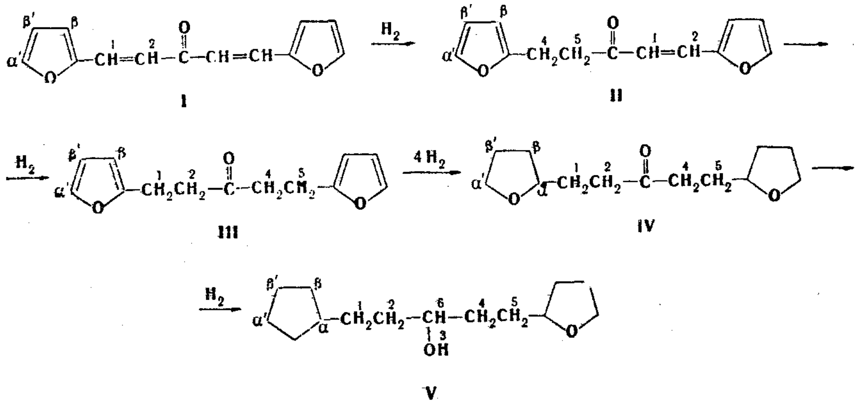
TABLE 1. PMR Spectra of Difurfurylideneacetone and Its Hydrogenation Products

Compound	Chemical shifts, δ, ppm									
	1-H	2-H	3-H	4-H	5-H	6-H	α′	β′	β	α
I	7,4 d $J=15{,}0$ Hz	6,8 d					7,45 m	6,4 m	6,6 m	
II	7,20 d $J=16{,}0$ Hz	7,05 d		2,8 s			6,43 m	5,95 m	6,58 m	
III				2,6 t			7,1 m	6,1 m	5,8 m	
IV				2,6 m			1,7 m	2,4 m		3,6 m
V	1,55 m		3,3 s	1,8 m		3,8 m	3,70 m	1,55 m		3,75 m

The formation of ketone II under similar conditions was not noted in [3-5], probably because of the ease of its subsequent transformations. The percentage of enone II in the catalyzate as a function of the temperature and the nature of the solvent ranges from 35 to 65%. The products of its subsequent transformations – 1,5-difurylpentan-3-one (III), 1,5-ditetrahydrofurylpentan-3-one (IV), and 1,5-ditetrahydrofurfurylpentan-3-ol (V) – then begin to appear. When 470 ml of H_2 (a hydrogen equivalent of 1568 ml) is absorbed by the catalyzate, starting I is used up completely; however, the rate of formation of ketone III remains constant for a certain time, and this constitutes evidence that starting ketone I does not participate in its formation. In precisely the same way, the exhaustion of I and II does not have a substantial effect on the rate of formation of ketone IV. The start of the intensive formation of alcohol V coincides with the start of the decrease in the amount of ketone IV.

Thus, the sequence of the formation of the products of hydrogenation of dienone I under the investigated conditions can be expressed by the scheme



Other things being equal, a change in the concentration from 0.15 to 0.62 mole/liter showed that the rate of hydrogen absorption does not depend on the concentration of starting I. This fact constitutes evidence that the reaction is zero-order in the starting compound.

An increase in the temperature leads to an increase in the rate of hydrogenation of dienone I. The rate increases particularly appreciably in the case of hydrogenation of the ethylene bonds in the side chain. The rate-determining step of the process is the reduction of the carbonyl group. The dependence of the logarithm of the rate constant on the reciprocal of the temperature is presented in Fig. 2. The activation energy found for 20-65°C is 6.2 ± 0.5 kcal/mole.

The set of data obtained make it possible to conclude that the hydrogenation of difurfurylideneacetone in the presence of a Raney nickel catalyst is realized in the following sequence: The ethylene bonds in the side chain are initially hydrogenated, the C=C bonds of the furan rings are then hydrogenated, and, finally, the carbonyl group is hydrogenated.

EXPERIMENTAL

The IR spectra of liquid films of the compounds were recorded with an IKS-14 spectrometer, and the PMR spectra of CCl_4 solutions of the compounds were recorded with a Jeol C-60 spectrometer with hexamethyldisiloxane as the internal standard. The mass spectra were re-

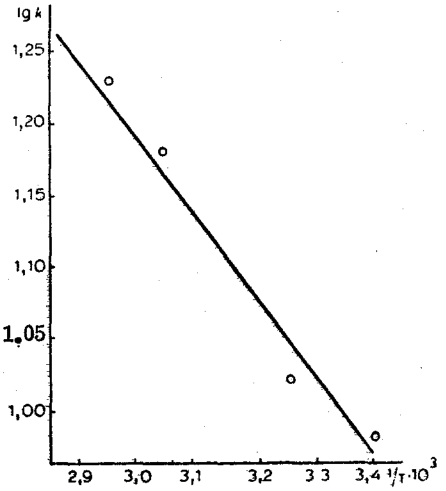


Fig. 2. Dependence of the logarithm of the rate constant of the reaction on the reciprocal of the temperature.

corded with a Varian-MAT CH-6 spectrometer with direct introduction of the substances into the ion source. The hydrogenation products were identified by means of genuine samples and from their spectra.

The starting difurfurylideneacetone was synthesized by the method in [7]. The Raney nickel catalyst was prepared by alkalization of an Ni—Ti—Al alloy (47:3:50%, respectively) with a 2% solution of sodium hydroxide at 96°C for 2 h. It was then washed with distilled water to pH 7. The catalyzate and individual products were analyzed chromatographically with a Tsvet-100 chromatograph (with a flame-ionization detector) with a 1 m by 4 mm column and a stationary phase consisting of 20% SKTFT-100 (methyltrifluoropropylsiloxane rubber) on Chromaton N.

Hydrogenation was carried out at 20-65°C in a catalytic hydrogenation flask (800-850 oscillations/min) in C_1-C_4 alcohols, dimethylformamide (DMF), and ethyl acetate. The volume of the solvent in all of the experiments was 30 ml for 2.14 g (0.01 mole) of dienone I. A weighed sample (0.40 g) of the catalyst was used once. A thermostated catalytic hydrogenation flask was charged with 0.40 g of the catalyst, 2.14 g (0.01 mole) of I, and 30 ml of the appropriate solvent; and the reaction was carried out in a hydrogen atmosphere with vigorous stirring for 3 h. The electrolytic hydrogen used was passed through concentrated sulfuric acid.

After absorption by the catalyzate of each 100 ml of hydrogen, a sample was withdrawn from the flask with a syringe for chromatographic analysis. A chromatographic column with a length of 1 m and a diameter of 18 mm and two-thirds filled with SKS activated silica gel (0.05-0.09 mm particles) was used for the separation of the hydrogenation products. The PMR spectra of the products are presented in Table 1.

1,5-Difurylpent-1-en-3-one (II). This compound had bp 138°C (3 mm) and mp 37°C (from heptane). Found: M$^+$ 216, $C_{13}H_{12}O_3$. Calculated: M 216. IR spectrum: 887, 1110, and 1280 (furan ring); 1520 (side chain C=C); 1620 cm^{-1} (C=O). An authentic sample was obtained by condensation of 1-(α-furyl)butan-3-one with furfural by a known method [8], which, in addition to ketone II, gives its isomer — 1-(α-furyl)-2-(α-furfurylidene)butan-3-one (VI), the structure of which was confirmed by its PMR spectrum.

1,5-Difurylpentan-3-one (III). This compound has by 134°C (3 mm), n_D^{20} 1.5022, and d_4^{20} 1.1017. Found: M$^+$ 218. $C_{13}H_{14}O_3$. Calculated: M 218. IR spectrum: 735, 895, 1240, and 1515 (furan ring): 1725 cm^{-1} (C=O). According to the data in [8], this compound has bp 136.5°C (3.5 mm), n_D^{20} 1.5025, and d_4^{20} 1.1011.

1,5-Ditetrahydrofurylpentan-3-one (IV). This compound has bp 130°C (2 mm), n_D^{20} 1.4780, and d_4^{20} 1.0471. Found: M$^+$ 226. $C_{13}H_{22}O_3$. Calculated: M 226. IR spectrum: 910, 1010, and 1101 (tetrahydrofuran ring); 1746 cm^{-1} (C=O). According to the data in [8], this compound has bp 128°C (2 mm) n_D^{20} 1.4785, and d_4^{20} 1.0476.

1,5-Ditetrahydrofurylpentan-3-ol (V). This compound has bp 145-147°C (1 mm), n_D^{20} 1.4790, and d_4^{20} 1.0350. Found: M$^+$ 228. $C_{13}H_{24}O_3$. Calculated: M 228. IR spectrum: 990, 1070, 1180, 2885, and 2960 (tetrahydrofuran ring); 3460 cm^{-1} (OH). According to the data in [8], this compound has bp 132-134°C (0.18 mm), n_D^{20} 1.4793 and d_4^{20} 1.0354.

LITERATURE CITED

1. I. F. Bel'skii and V. M. Shostakovskii, Catalysis and the Chemistry of Furan [in Russian], Nauka, Moscow (1972), p. 44.
2. G. W. Johnson, British Patent 476189 (1937); Chem. Abstr., 32, 3857 (1938).
3. P. Thomas, Bull. Soc. Chim. Fr., No. 4, 529 (1954).
4. R. Cornubert and I. C. Phelisse, Compt. Rend., 229, 460 (1949).
5. R. Cornubert and I. C. Phelisse, Compt. Rend., 227, 1131 (1948).
6. Yu. M. Mamatov, R. Mat'yakubov, N. Kh. Mukhamadaliev, and E. G. Abduganiev, Khim. Tekhnol. Furanovykh Soedin. Tr. Kubansk. Gos. Univ., Krasnodar, 256, 13 (1977).
7. I. V. Kamenskii and N. V. Ungurean, Plastmassy, No. 8, 17 (1960).
8. A. D. Petrov, V. G. Glukhovtsev, and S. V. Zakharova, Dokl. Akad. Nauk SSSR, 153, 1346 (1963).

METHOD FOR PREPARATION OF METHYL 3-(2,2-DIMETHYL-4-TETRAHYDROPYRANYL)-3-OXOPROPIONATE

R. S. Vartanyan, Zh. V. Kazaryan,
A. P. Engoyan, and S. A. Vartanyan

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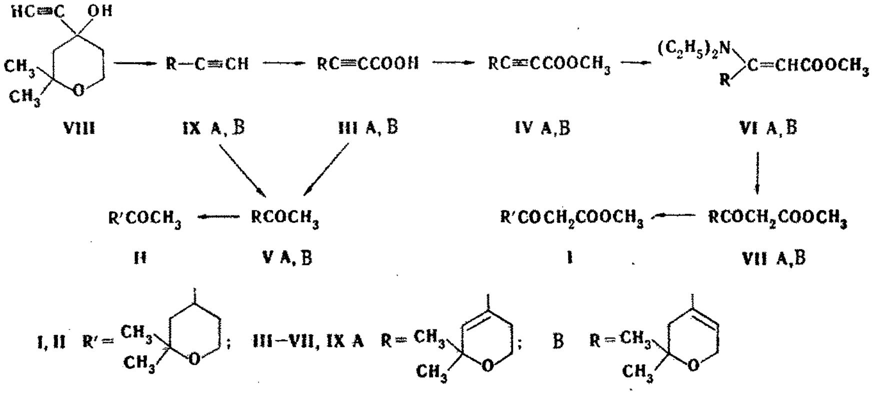
A method is proposed for the synthesis of methyl 3-(2,2-dimethyl-4-tetrahydropyranyl)-3-oxopropionate on the basis of 2,2-dimethyl-4-ethynyltetrahydro-4-pyranol.

β-Keto esters are practically universal starting compounds for the most diverse synthesis in all fields of organic chemistry and particularly in the chemistry of synthetic medicinal substances. In the present communication we propose a method for the synthesis of methyl 3-(2,2-dimethyl-4-tetrahydropyranyl)-3-oxopropionate (I). Attempts to synthesize keto ester I from 2,2-dimethyl-4-cyanotetrahydropyran and zincobromacetic ester [1, 2] by carbalkoxylation [3, 4] of 2,2-dimethyl-4-acetyltetrahydropyran (I) with diethyl carbonate in the presence of a number of basic agents, by acylation [5] of acetoacetic ester with 2,2-dimethyltetrahydropyran-4-carboxylic chloride, and by carboxylation [6] of ketone II with methoxymagnesium methylcarbonate were unsuccessful. An attempt to directly hydrate acetylenecarboxylic acids III and their esters IV in the presence of mercury catalysts, concentrated sulfuric acid, and alkali was also unsuccessful [7]. Ketones V were obtained in this case under acidic conditions. Indirect hydration IV → VII [7], on the basis of which the synthesis of keto ester I was also developed, proved to be extremely effective:



The dehydration of alcohol VIII [8] to a mixture of isomeric ethynyldihydropyrans IX was accomplished by a known method [9]. In the course of the entire synthesis the work was carried out with a mixture of isomers A and B, the ratio of which was determined both by gas–liquid chromatography (GLC) and PMR spectroscopy (Table 1).

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