ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 2, pp. 226–233. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © O.V. Fedorova, M.S. Valova, Yu.A. Titova, I.G. Ovchinnikova, A.N. Grishakov, M.A. Uimin, A.A. Mysik, A.E. Ermakov, G.L. Rusinov, V.N. Charushin, 2011, published in Kinetika i Kataliz, 2011, Vol. 52, No. 2, pp. 234–241.

Catalytic Effect of Nanosized Metal Oxides in the Biginelli Reaction

O. V. Fedorova, M. S. Valova, Yu. A. Titova, I. G. Ovchinnikova, A. N. Grishakov, M. A. Uimin, A. A. Mysik, A. E. Ermakov, G. L. Rusinov, and V. N. Charushin

I. Postovsky Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620041 Russia

e-mail: fedorova@ios.uran.ru

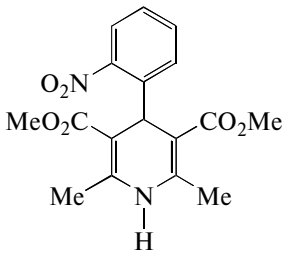
Received March 2, 2010

Abstract—The effect of nanosized metal oxides on the regio- and stereoselectivity of the multicomponent Biginelli reaction and the reaction mechanism under conditions of heterogeneous catalysis were studied. It was found that the considerable activation of reagents occurred on the surface of metal nanooxides. The Biginelli reaction occurred by two mechanisms: a carbocationic mechanism took place along with the generally accepted mechanism (through the *N*-acyliminium ion). Nanosized metal oxides in the presence of chiral inductors increased the regio- and stereoselectivity of the Biginelli reaction.

DOI: 10.1134/S0023158411020066

INTRODUCTION

4-Aryl-substituted dihydropyrimidines are close structural analogs of calcium channel blockers like nifedipine (**1**) or nitrendipine (**2**), which are used in treatment for cardiovascular diseases [1, 2]. 4-Aryl-substituted dihydropyrimidines exhibit high activity as antihypertensive agents (**3**), α_{1a} adrenergic antagonists (**4**), and antitumor agents (**5**), which act as cell division blockers [3–5].



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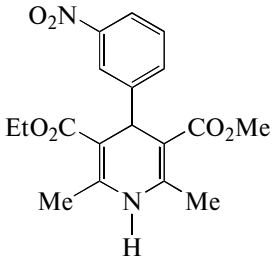

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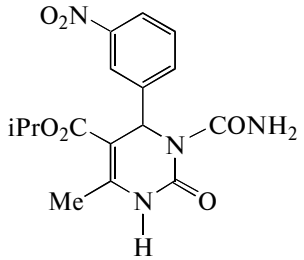

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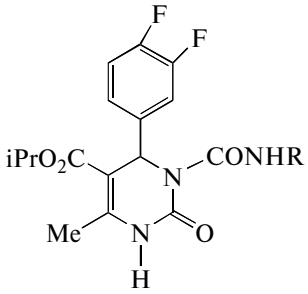

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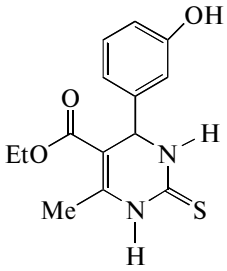


5
Monastrol

The multicomponent Biginelli reaction, which consists in the cyclocondensation of an aldehyde, a β-ketoester, and urea (thiourea) on heating in an acidic medium, is used to prepare these compounds (Scheme 1). However, high regioselectivity was reached only with the use of a limited range of starting reagents. Thus, the yield of target products dramatically decreased if a substituted aromatic aldehyde participated in the

reaction. Therefore, a search for optimum catalysts for the Biginelli reaction is a problem of considerable current interest.

The greatest number of publications concerning this problem was devoted to choosing various Lewis acids, for example, BF_3–OEt_2, in combination with transition metal salts [3], $FeCl_3$ [4], $InCl_3$ [5], $LaCl_3 \cdot 7H_2O$ [6], lanthanides, or copper triflate [7, 8]. In some well-known examples, the Biginelli reaction was performed in the presence of a heterogeneous catalyst [9–11].

On the other hand, chiral Lewis acids were used in the asymmetric multicomponent synthesis of Biginelli compounds whose pharmacological properties depend on the absolute configuration of the C4 stereogenic center [6]. For example, *R*-enantiomer SQ 32926 (**3**) exhibited an antihypertensive activity 400 times higher than that of the *S*-enantiomer [3]. Therefore, methods for the asymmetric synthesis of these heterocycles are currently under intense study [8].

An example of the use of nanosized magnesium oxide in combination with a chiral inductor in the asymmetric Claisen–Schmidt reaction (with the participation of α,β-unsubstituted ketones) is well known [12]. Previously, we studied the effect of nanosized metal oxides (metal nanooxides) on the stereoselectivity of the Hantzsch reaction [13]. Here, we consider the use of metal nanooxides (in the presence of chiral inductors) as new catalysts for the Biginelli reaction. The adsorption of reactants and chiral inductors on the nanooxides of copper and aluminum was studied by IR spectroscopy. The composition of crude reaction products was studied using ^{1}H NMR spectroscopy and HPLC.

EXPERIMENTAL

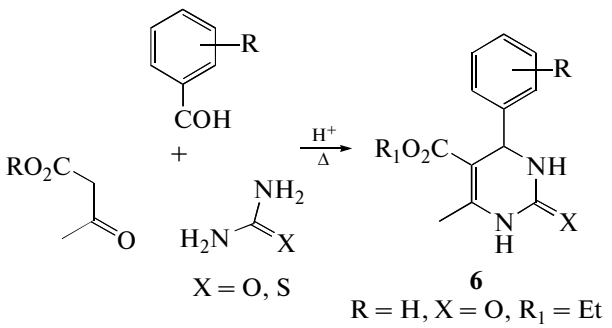
Reagents and Analytical Techniques

Urea (99%), benzaldehyde (99%), and 3-nitrobenzaldehyde (99%) from Lancaster; ethyl acetoacetate (99%) from Acros Organics; and diethylene glycol and PEG 200 polyethylene glycol from Merk were used in this study. Aluminum oxide Al_2O_3 (analytical grade) and copper oxide CuO (chemically pure) from Khimsnab and metal nanooxides with a particle size of 50–80 nm, which were prepared by gas-phase (Al_2O_3, MgO, NiO, ZnO, and CuO) [14] or sol–gel (TiO_2) [15] methods, served as catalysts.

A Boetius hot stage was used to measure melting points (mp); the results were used without additional correction.

Diffuse reflectance spectra were measured on a Spectrum One Fourier transform IR spectrometer (PerkinElmer) equipped with an automated diffuse reflectance attachment.

The ^{1}H NMR spectra were obtained on an AVANCE DRX-400 spectrometer (Bruker) with an operating frequency of 400.13 MHz (internal standard, TMS).



Scheme 1. Biginelli reaction.

An enantiomeric excess in the Biginelli reaction products was determined by HPLC using a Chiracel OD-H chiral column and a UV–visible detector (254 nm). A mixture of hexane with 2-propanol (85 : 15) was used as an eluant; the elution rate was 1.0 ml/min.

Determination of the Regioselectivity of the Biginelli Reaction Occurring in the Presence of Metal Nanooxides

Benzaldehyde (1.06 g, 10 mmol) and ethyl acetoacetate (1.30 g, 10 mmol) were mixed, and ethanol (10 ml) and 1.0 mmol of a metal nanooxide were added. The reaction mixture was stirred for 1 h at 22–25°C; thereafter, urea **3** (0.6 g, 10 mmol) was added. The reaction mixture was stirred at 50 or 70°C for 3–20 h, and the solvent was distilled off. The crude product was analyzed by ^{1}H NMR spectroscopy. If necessary, the crude product was purified on a chromatographic column (SiO_2; eluant: a mixture of hexane with ethyl acetate in a ratio of 1 : 5). Resulting compound **6** had mp 204–206°C (according to published data [12], mp 207–208°C).

^{1}H NMR spectrum in DMSO-d_6 (δ, ppm): 9.18 (br s, 1H), 7.72 (s, 1H), 7.22–7.34 (m, 5H), 5.14 (d, 1H, J = 3.3 Hz), 3.98 (q, 2H, J = 7.08 Hz), 2.25 (s, 3H), 1.09 (t, 3H, J = 7.08 Hz).

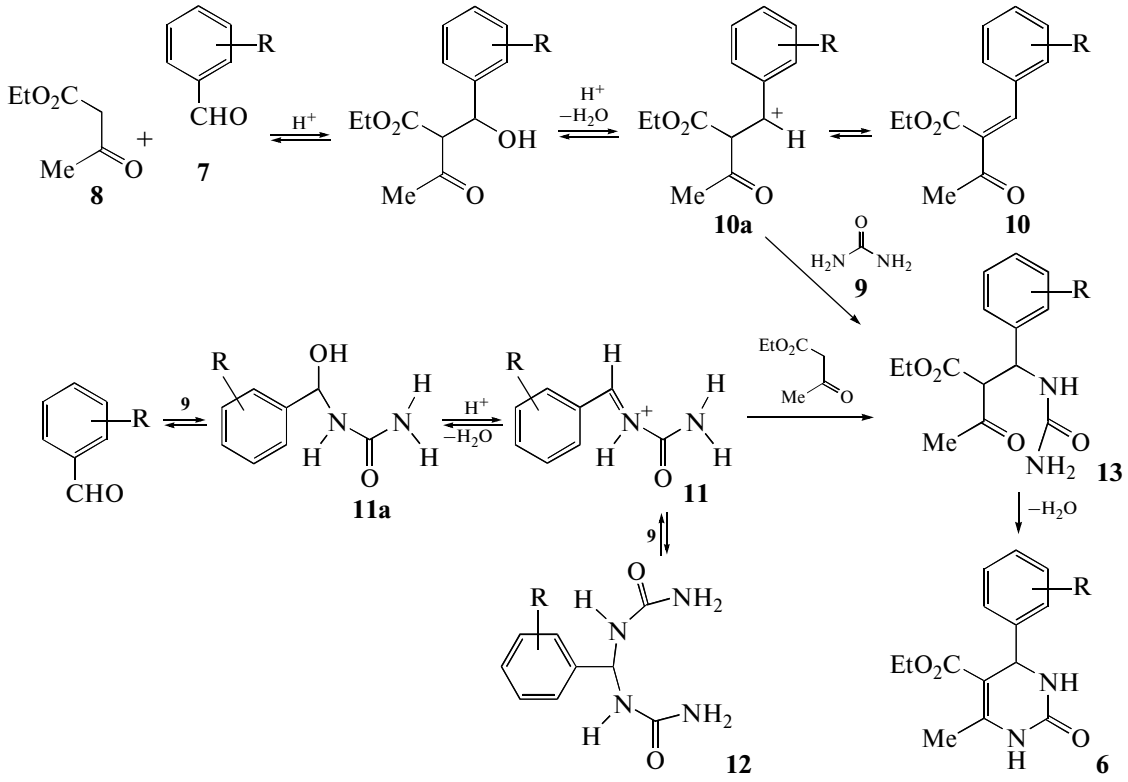
IR spectrum (ν, cm^{-1}): 3244, 1703, 1650, 1465, 1224, 1091, 782, 758, 699, 516.

Compound **13** (see Scheme 2): mp 155–157°C (according to published data [16], mp 156–158°C).

For $C_{11}H_{24}N_8$ anal. calcd. (%): C, 49.23; H, 9.01; N, 41.75.

Found (%): C, 49.18; H, 8.87; N, 41.43.

^{1}H NMR spectrum (δ, ppm): 8.79 (s, 1H), 7.21–7.07 (m, 5H), 4.85 (s, 1H), 4.02–3.93 (q, q, 4H, J = 7.08 Hz), 2.25 (s, 6H), 1.12 (t, 6H, J = 7.08 Hz).



Scheme 2. Biginelli reaction mechanisms.

IR spectrum (ν, cm^{-1}): 3341, 3237, 3060, 3089, 1686, 1453, 1487, 1648, 1090, 1123, 1208, 1247, 767, 738, 702, 680, 574, 500.

Analysis of the ^1H NMR Spectra of Crude Reaction Products

The ratio between target product **6**, intermediates **10** and **12** (see Scheme 2), and by-product **13** (dihydropyridine) was determined from the integrated intensities of the main signals of protons in the ^1H NMR spectrum (Table 1).

Table 1. Main proton signals of compounds **6**, **10**, **12**, and **13**

Product	Proton signals δ, ppm			
	NH_2	NH	CH	Me
6a	–	9.21	5.15	2.25
10	–	–	7.48 (*Z*-isomer)	2.42 (*Z*-isomer)
			7.47 (*E*-isomer)	2.35 (*E*-isomer)
12	5.68	6.73	6.14	–
13	–	8.80	4.86	–

Determination of the Stereoselectivity of the Biginelli Reaction Performed in the Presence of Metal Nanooxides and Chiral Inductors

Benzaldehyde (1.06 g, 10 mmol), ethyl acetoacetate (1.30 g, 10 mmol), 1.0 mmol of a chiral inductor, and 1.0 mmol of a metal nanooxide were mixed. Then, 15.0 ml of a solvent was added, and the contents were stirred for 1 h at 22–25°C; thereafter, urea **3** (0.6 g, 10 mmol) was entered. The reaction mixture was stirred at 22 or 50°C for 22–50 h, and the solvent was distilled off. Crude product **6a** was analyzed by ^1H NMR spectroscopy and HPLC. The retention times of the *S*- and *R*-enantiomers were 13.86 and 16.63 min, respectively.

*Synthesis of Bis-ureide (**12**)*

Benzaldehyde (1.06 g, 10 mmol), urea (1.20 g, 20 mmol), and 3–4 drops of HCl in 140 ml of ethanol were mixed. The reaction mixture was stirred for 5 h, and the resulting product was filtered off and dried in air. 1.60 g (77%) of compound **12** with mp 225–226°C was obtained (according to published data [17], mp 224–226°C).

For $C_9H_{12}N_4O_2$ anal. calcd. (%): C, 51.92; H, 5.77; N, 26.92.

Found (%): C, 52.08; H, 5.87; N, 26.83.

Table 2. Effect of the nature of a catalyst (nanosized metal oxide) and a solvent on the yield of racemic dihydropyrimidinone **6**

Experiment no.	Catalyst*	Solvent	Temperature, °C	Time, h	Yield, %
1	HCl	Ethanol	70	3	78
2	HCl	Ethanol	70	10	86
3	Al_2O_3	Ethanol	70	3	31
4	Al_2O_3	Ethanol	70	8	55
5	Al_2O_3	Ethanol	70	20	87
6	Al_2O_3	Methanol	50	20	82
7	Al_2O_3	Acetic acid	70	8	79
8	Al_2O_3	Diethylene glycol	50	20	78
9	Al_2O_3	PEG 200	50	20	78
10	CuO	Ethanol	70	15	65
11	TiO_2	Ethanol	70	20	74
12	ZnO	Ethanol	70	20	75
13	Al_2O_3 (bulk)	Ethanol	70	20	50
14	CuO (bulk)	Ethanol	70	20	43

* Concentration: 10 mol %.

^{1}H NMR spectrum (δ, ppm): 7.96–7.26 (m, 5H), 6.72 (d, 2H, J = 8 Hz), 6.14 (t, 1H, J = 8 Hz), 5.68 (br s, 4H).

*Synthesis of Ethyl 2-Acetyl-3-Phenylacrylate (**10**, R = H)*

Compound **10** as a mixture of *E*- and *Z*-isomers (50 : 50) was prepared in accordance with a published procedure [12]. It was also synthesized by another procedure in the presence of aluminum nanooxide. In this case, 1–2 drops of morpholine was added to a mixture of benzaldehyde **7** (0.5 g, 3.3 mmol), ethyl acetoacetate **8** (1.15 g, 9.9 mmol), and 0.33 mmol of the metal nanooxide in 3 ml of acetonitrile, and the contents were stirred at 60°C for 15 h. The resulting product had a consistence of oil.

For $C_{13}H_{14}O_3$ anal. calcd. (%): C, 71.56; H, 6.42.

Found (%): C, 71.48; H, 6.57.

^{1}H NMR spectrum of *Z*-isomer (δ, ppm): 7.48 (s, 1H), 7.45 (m, 5H), 4.32 (q, 1H, J = 7 Hz), 2.42 (s, 3H), 1.27 (t, 3H, J = 7 Hz). ^{1}H NMR spectrum of *E*-isomer (δ, ppm): 7.47 (s, 1H), 7.39 (m, 5H), 4.31 (q, 1H, J = 7 Hz), 2.35 (s, 3H), 1.33 (t, 3H, J = 7 Hz).

According to ^{1}H NMR-spectroscopic data, the ratio between the *E*- and *Z*-isomers was 1 : 2.

Adsorption

The adsorption of the staring reactants of the Biginelli reaction on metal nanooxides was performed from sorbate solutions in methanol (at a sorbate : sorbent molar ratio of 1 : 3) with the subsequent removal of the solvent.

RESULTS AND DISCUSSION

As found previously, both active Lewis acid sites and Brønsted acid and basic sites occur on the surface of metal nanooxides [13]. Because the nature of the surface has a considerable effect on the catalytic properties of metal nanooxides, we studied the synthesis of racemic dihydropyrimidinone **6** on various nanooxides (copper, aluminum, titanium, and zinc). The reaction was performed in four different solvents. Table 2 summarizes the results. It also contains data on the comparative catalytic activity of nanosized and bulk metal oxides. The yield of target product **6** on bulk oxides was lower than that on nanosized oxides by a factor of 1.5–1.7 (Table 2, experiments 13 and 14). This can be explained by a lower sorption capacity of bulk samples, as compared with that of nanosized oxides [13].

Under conditions of heterogeneous catalysis, the rate of the Biginelli reaction decreased; however, an increase in the reaction time to 15–20 h makes it possible to obtain product **6** in 65–87% yield. Better results were obtained with the use of nanosized Al_2O_3; in this case, the selectivity was also higher. An analysis of the ^{1}H NMR spectra indicated that 5–10% of unidentified impurities were detected among the reaction products obtained in the absence of nanosized oxides (Table 3, experiment 10). They were not formed in the presence of nanosized metal oxides.

Note that reaction intermediates were unusually stabilized under conditions of heterogeneous catalysis (Table 3). This allowed us to study the mechanism of the Biginelli reaction by analyzing the ^{1}H NMR spectra of crude reaction products.

Table 3. Composition of the crude products of the Biginelli reaction according to ^{1}H NMR-spectroscopic data (reaction time, 8 h)

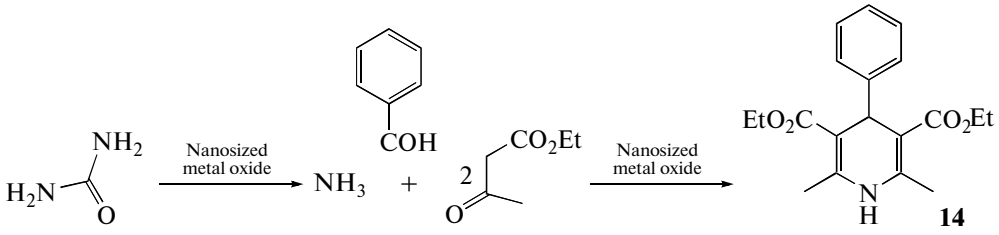
Experiment no.	Catalyst	Catalyst amount, mol %	Solvent	Relative concentration, %			
				6	**14**	**12**	**10**
1	ZnO	10	Ethanol	70	9	4	17
2	CuO	10	Ethanol	44	Traces	Traces	56
3	Al_2O_3	10	Ethanol	55	11	Traces	34
4	Al_2O_3	10	Acetic acid	79	4	Traces	17
5	TiO_2	10	Ethanol	74	Traces	12	14
6	TiO_2	50	Ethanol	70	7	Traces	23
7	TiO_2	100	Ethanol	48	52	Traces	Traces
8	TiO_2, modified with phosphoric acid	10	Ethanol	78	0	9	13
9	MgO	10	Ethanol	23	7	0	70
10	HCl	5	Ethanol	80	Traces	Traces	12

Two mechanisms of the Biginelli reaction have been described in the literature (Scheme 2). The first carbocationic mechanism, which involves the formation of carbocation **10a**, was proposed by Sweet and Fissekis [18]. In 1997, Kappe [19], who studied in detail the Biginelli condensation reaction, proposed another mechanism. The addition of urea to benzaldehyde under conditions of acid catalysis resulted in the formation of *N*-(1-hydroxybenzoyl)urea **11a** as a result of an ordinary nucleophilic attack. This intermediate compound underwent dehydration in the presence of an acid with the formation of ion **11**, which can be considered as a highly reactive *N*-acyliminium ion. Then, ethyl acetoacetate **8** added as a π nucleophile to *N*-acyliminium ion **11** to form intermediate **13**, which subsequently underwent cyclization to target compound **6**. Therefore, Kappe recommended loading reagents into the reactor in the following order: initially, aldehyde **7**; then, urea **9**; and, finally, ethyl acetoacetate **8**.

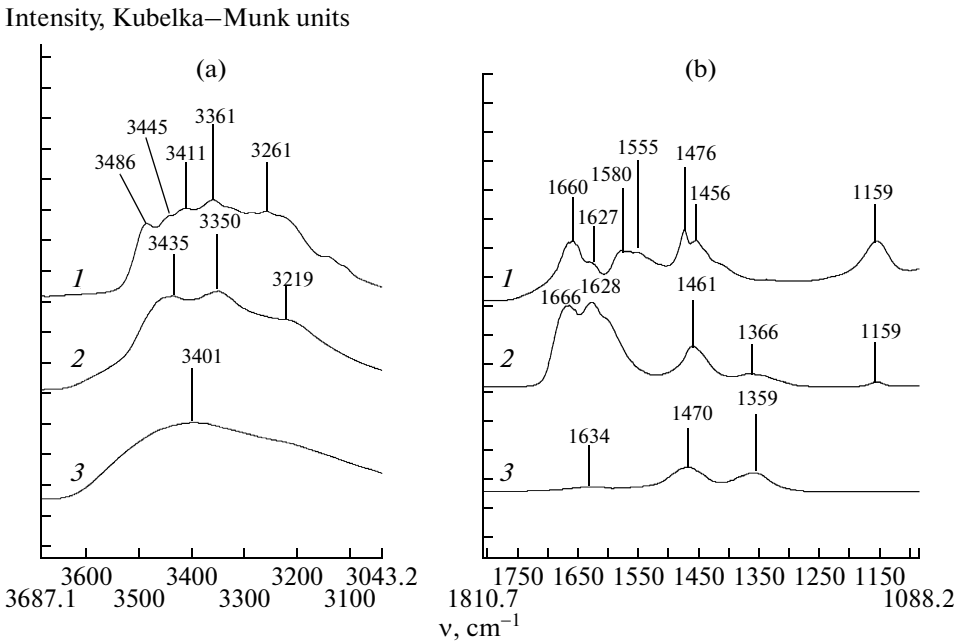
It was found that adducts **10** and **12** (products of the interaction of *N*-acyliminium ion **11** with urea) were formed in the course of the reaction because their traces were detected in the ^{1}H NMR spectra of all of the crude products (Table 3). Consequently, the Biginelli reaction occurred by both of the mechanisms under conditions of heterogeneous catalysis (in the presence of metal nanooxides). However, because the amount of intermediate **10** was always larger than that of intermediate **12**, we can hypothesize that the carbocationic mechanism was predominant. Evidently, this is a reason for decreasing the rate of the Biginelli reaction under conditions of heterogeneous catalysis. It is likely that the ratio between isomers depended on the ratio between acid and basic sites on the catalyst surface.

In addition, the ^{1}H NMR spectra of crude products **6** exhibited the proton signals of dihydropyridine **14**; that is, the Biginelli reaction was accompanied by the Hantzsch reaction under conditions of heterogeneous catalysis (Scheme 3). This can be clearly seen with the use of titanium oxide as a catalyst because an increase in its concentration in the reaction mixture caused an increase in the yield of dihydropyridine **14** (Table 3, experiments 5–7). On titanium nanooxide modified with phosphoric acid (because of this, it had acid sites), the reaction was shifted toward the formation of dihydropyrimidine **6** (Table 3, experiment 9).

On going from nanosized to bulk oxides, the yield of dihydropyridine **14** increased. Thus, the ratios between Biginelli and Hantzsch reaction products were 1.0 : 0.1 and 1.0 : 0.2 in the presence of nanosized and bulk Al_2O_3, respectively.



Scheme 3. Hantzsch reaction on nanosized metal oxides.



IR spectra of (*1*) urea, (*2*) urea adsorbed on CuO, and (*3*) CuO nanooxide in the most informative ranges of (a) 3687–3043 and (b) 1810–1088 cm^{-1}.

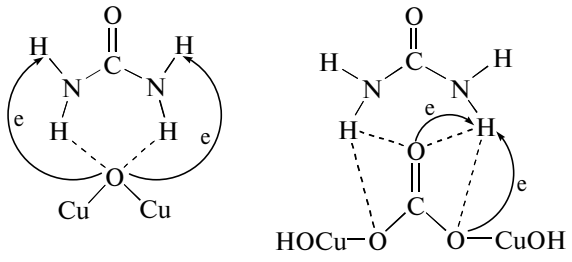
The Biginelli reaction performed under conditions of microwave irradiation on silica gel resulted in the predominant formation of Hantzsch reaction products [14]. Our results suggest that the occurrence of the Hantzsch reaction was due to surface properties rather than the action of microwave irradiation.

Previously, we found that the classical Biginelli reaction (in an ethanol solution with HCl as a catalyst) can be accelerated by ultrasonication [20]. The Biginelli compounds were formed in 90–95% yield for a few minutes; in this case, Hantzsch reaction products were not detected.

The adsorption of Biginelli reaction components on copper and aluminum nanooxides was studied by IR spectroscopy. Coordination between benzaldehyde and ethyl acetoacetate, which led to their activation on the surface of these nanooxides, was described previously [13]. The main absorption bands of the resulting surface compounds were specified in the cited publication.

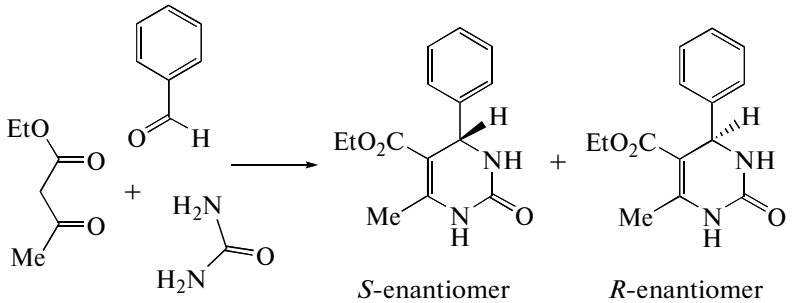
Urea reacts with the surface of nanooxides through a hydrogen atom of the NH_2 group. This is evidenced by shifts in δ_{N-H} absorption bands on copper and aluminum oxides by 49 and 26 cm^{-1}, respectively (see the figure). The absorption bands of hydroxycarbonate oxygen atoms on the surface of copper at 1470 and 1359 cm^{-1} were shifted to 1460 and 1366 cm^{-1}, respectively. Scheme 4 shows why urea adsorption on the surface of metal nanooxides increased its reactivity in the Biginelli reaction. Fedorova et al. [13] found that the coordination of key intermediate **10** ($R = NO_2$) of the Biginelli reaction on the surface occurred through the oxygen atoms of carbonyl and ester groups to facilitate an increase in its reactivity.

We studied the formation of key intermediate **10** (R = H) on metal nanooxides and found that, in the presence of aluminum nanooxide, the ratio between isomers changed in favor of the *Z*-isomer (2 : 1), whose structure is most favorable for the formation of the *S*-enantiomer of compound **6**. These results allowed us to hypothesize that nanosized metal oxides can facilitate the stereoselective synthesis of Biginelli compounds. Nanosized CuO, Al_2O_3, ZnO, NiO, and MgO were tested as catalysts, whereas *L*-tartaric acid, *L*-proline, and quinine sulfate served as chiral inductors. These chiral inductors in the absence of metal nanooxides had no effect on the stereoselectivity of the Biginelli reaction. The combined use of a heterogeneous catalyst and a chiral inductor allowed us to change the ratio between stereoisomers by >20% in favor of the *S*-isomer in some experiments (Table 4, experiments 13–15). Better results were obtained with



Scheme 4. Interaction of urea with copper nanooxide.

Table 4. Synthesis of dihydropyrimidine in the presence and absence of nanosized metal oxides



S-enantiomer *R*-enantiomer

Experiment no.	Catalyst	Chiral inductor	Solvent	Temperature, °C	Yield, %	*S* : *R* enantiomer ratio
1	–	*L*-Tartaric acid	EtOH	50	75	50 : 50
2	CuO	–	EtOH	50	70	50 : 50
3	CuO	*L*-Tartaric acid	EtOH	50	75	50 : 50
4	–	*L*-Proline	MeOH	50	76	50 : 50
5	CuO	*L*-Proline	MeOH	50	76	56 : 44
6	Al_2O_3	*L*-Proline	MeOH	50	78	55 : 45
7	ZnO	*L*-Proline	MeOH	50	70	55 : 45
8	NiO	*L*-Proline	MeOH	50	71	58 : 42
9	MgO	*L*-Proline	MeOH	50	70	58 : 42
10	TiO_2	*L*-Proline	MeOH	50	68	50 : 50
11	Al_2O_3	Quinine sulfate	MeOH	50	56	59 : 41
12	MgO	Quinine sulfate	CH_3CN	22	62	58 : 42
13	NiO	Quinine sulfate	DMF	22	72	61 : 39
14	NiO	Quinine sulfate	MeOH	50	77	61 : 39
15	MgO	*L*-Proline	H_2O	50	57	62 : 38

Note: Reaction time, 20–25 h; catalyst and chiral inductor concentrations, 10 mol % each.

the use of nanosized MgO as a catalyst, *L*-proline as a chiral inductor, and H_2O as a solvent. This fact is of special interest because, as a rule, nonpolar solvents are used to improve stereoselectivity under homophase conditions.

The ratio between enantiomers was determined by HPLC. The absolute configuration of enantiomers in compound **6** was found using published data [21] and the results of X-ray diffraction analysis. In the course of the synthesis of **6** in the presence of *L*-tartaric acid and copper nanooxide (Table 4, experiment 3), *S*-enantiomer prisms were separated from the needle-shaped crystals of the enantiomer mixture.

A metal nanooxide in the presence of a chiral inductor increased not only the stereoselectivity but also the regioselectivity of the test reaction. With the use of *L*-tartaric acid or *L*-proline as a chiral inductor, the formation of compound **14** (Hantzsch reaction product) was not observed. If quinine sulfate was a chiral inductor, trace amounts of compound **14** were formed, as evidenced from an analysis of the ^{1}H NMR spectrum of the crude product.

In the spectra of the majority of crude products, only the signals of target product **6** were present in addition to the proton signals of intermediates **10** and **12**.

Thus, metal nanooxides, which are responsible for the activation of starting reagents and key intermediate **10**, are efficient catalysts for the Biginelli reaction. The combined use of a heterogeneous catalyst and a chiral inductor (*L*-tartaric acid, *L*-proline, or quinine sulfate) facilitates an increase in both the regioselectivity and the stereoselectivity of the reaction.

ACKNOWLEDGMENTS

We are grateful to Dr. Sci. (Chem.) L.A. Petrov (Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences) for providing us with the samples of nanosized titanium oxide and to Cand. Sci. (Chem.) P.A. Slepukhin (Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences) for performing X-ray diffraction analysis.

This work was supported by the Council of the President of the Russian Federation for Support of Leading Scientific Schools (grant no. NSh-65261.2010.3), the Presidium of the Ural Branch of the Russian Academy of Sciences (project nos. 09-P-23-2001, 09-I-3-2004, and 09-P-3-2001), the Russian Foundation for Basic Research (project nos. 07-03-9611-r_ural_a and 10-03-90026-Bel_a), and the Korea Atomic Energy Research Institute (contract no. 01/06 "Development of New Chiral Catalytic Systems Based on Nanocrystalline Metals and Metal Oxides").

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