

# Nucleophilic Addition to Acetylenes in Superbasic Catalytic Systems: XVII.\* Vinyl Ethers with Furyl and Cycloacetal Fragments: Synthesis and Structure

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**Abstract**—4-Hydroxymethyl-2-(2-furyl)-1,3-dioxolane and 5-hydroxy-2-(2-furyl)-1,3-dioxane consisting of mixtures of *cis*- and *trans*-isomers react with acetylene in the superbasic catalytic system KOH–DMSO at the atmospheric or higher pressure (80–85°C, 2–3 h) giving the corresponding vinyl ethers in 88–90% yield. The ratio of the structural and configurational isomers in vinyl ethers remains the same as in the initial compounds.

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The development of the organic synthesis based on the reproducible sources is among the priority tasks of the today chemistry. In this respect the attention of researchers is directed to glycerol, side product in the production of biodiesel fuel [2], and furfural formed in the hydrolysis of pentosan raw materials [3].

The glycerol cycloacetals are used in the medicine and veterinary as solvents in the preparation of parenteral drugs [4], and also in perfumery and cosmetics (they provide the transdermal delivery of the biologically active components [5]).

The furfural derivatives are used in the production of furan resins [6], adhesives, dyes [7], and the additives to the diesel fuels [8].

The reaction of furfural with glycerol (or the other polyhydric alcohols) is a known process [9, 10]. The reaction products, furyl-1,3-dioxacyclanes, possess a considerable synthetic and practical potential. This class of compounds contains the known pesticides “Furrolan” (2-furyl-1,3-dioxolane) [11] and “Krasnodar-1” [5-hydroxymethyl-5-ethyl-2-(2-furyl)-1,3-dioxane] [12] possessing growth regulating and fungicidal action.

A promising method of the synthesis of new derivatives of the furan 1,3-dioxacyclanes consists in direct

vinylation of hydroxy-containing cyclic acetals obtained from furfural and available polyhydric alcohols. The information on vinylation with acetylene of the glycerol cycloacetal derivatives is poor. A synthesis was described of 2,2-dialkyl-4-vinylloxymethyl-1,3-dioxolanes by the reaction of 2,2-dialkyl-4-hydroxy-methyl-1,3-dioxolanes with acetylene in the presence of KOH at heating (135–140°C) and high pressure (the initial pressure of acetulene 14–16 at) [13]. The nucleophilic addition of 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane to acetylene efficiently proceeded under relatively mild temperature conditions (KOH, 100–125°C, 1–2 h, initial pressure 11–12 at) and resulted in the corresponding functional vinyl ethers in a high yield [14].

The target of this study was the synthesis of unknown functionalized vinyl ethers with furan and acetal fragments based on the acetylene reaction with 4-hydroxymethyl-2-(2-furyl)-1,3-dioxolane (**I**) and 5-hydroxy-2-(2-furyl)-1,3-dioxane (**II**), which were easily obtained from glycerol and furfural in the presence of acid catalysts [9]. Initial compounds **I** and **II** were obtained in this study by heating (80°C) of glycerol and furfural in benzene in the presence of 4-methylbenzenesulfonic acid. The overall yield of compounds **I** and **II** was 76%, and their ratio in the mixture was ~1:1. Under these conditions the dioxolane derivative **I** formed as a mixture of equal

\* For Communication XVI, see [1].

amounts of *cis*- and *trans*-isomers whereas the ratio of *cis*- and *trans*-isomers in the disubstituted 1,3-dioxane **II** was ~1.5:1 (Scheme 1).

Compounds **I** and **II** materially do not react with acetylene under the common conditions of alcohol vinylation (50 mol% KOH, dioxane, 100°C, 2 h, initial pressure of acetylene 12 at). The use of the catalytic system KOH–DMSO made it possible to carry out this reaction in relatively mild conditions at the atmospheric pressure (80–85°C, 3 h, 50 mol% KOH, acetylene flow rate ~1 l/h) and to get 4-vinyloxymethyl-2-(2-furyl)-1,3-dioxolane (**III**) and 5-vinyloxy-2-(2-furyl)-1,3-dioxane (**IV**) in a ratio ~1 : 1 in an overall yield 90% (Scheme 2). The ratio of *cis*- and *trans*-isomers in the vinyl ethers **III** and **IV** obtained corresponded to that in the initial compounds.

At the high pressure (initial pressure of acetylene 14 at) similar results were as expected obtained in shorter time.

The reaction progress at the atmospheric pressure was monitored by the analysis of the reaction mixture by <sup>13</sup>C NMR spectroscopy. The formation of vinyl ethers **III** and **IV** was followed by the increase in the signals of the β-carbon atom of the vinyloxy groups (δ 87–90 ppm), and the conversion of initial compounds was observed by the disappearance of the resonance signals of the carbon atoms attached to the hydroxy groups (δ 60–65 ppm). The nearly equal amount of the formed vinyl ethers **III** and **IV** and also their high preparative yield indicate the comparable reactivity of the isomeric compounds **I** and **II** in the vinylation reaction.

The assignment of signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of vinyl ethers **III** and **IV** was carried out with the use of the double resonance and 2D correlation methods COSY, NOESY, HSQC/HMBC. The signals of all components were identified, but due to their partial

overlapping we did not analyze the multiplicity and the coupling constants.

The chemical shifts of the C<sup>2</sup> atom in the dioxane ring in both isomers of 5-vinyloxy-2-(2-furyl)-1,3-dioxane (**IV**) practically coincide (98 ppm) indicating the same orientation of the furyl substituent serving as a conformationally fixing group. The equatorial position of the furyl substituent is confirmed by the following data. In the NOESY spectrum cross-peaks were observed originating from the interaction between the axial protons H<sup>4,6</sup> and the acetal proton H<sup>2</sup> that corresponds to the axial orientation of the latter. This assignment may be performed also using the coupling constants <sup>13</sup>C–<sup>1</sup>H that considerably differ at the axial and equatorial orientation of the hydrogen atoms; these coupling constants are frequently applied to the estimation of the configuration of the anomeric centers in the saturated rings.

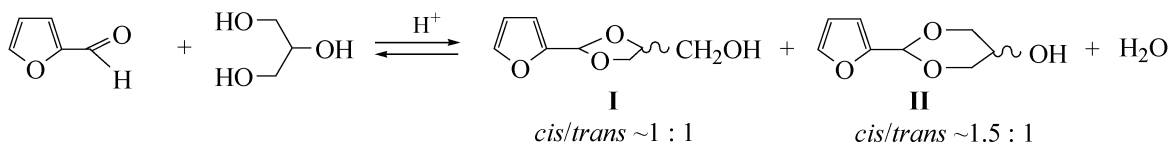
It was shown formerly that in unsubstituted 1,3-dioxanes [15, 16] the value <sup>1</sup>J(C<sup>2</sup>,H<sub>e</sub>) is by 10 Hz larger than <sup>1</sup>J(C<sup>2</sup>,H<sub>a</sub>) due to the so-called anomeric effect originating from the hyperconjugation interaction n<sub>O</sub> → σ\*(C–H<sub>a</sub>). The value <sup>1</sup>J(C<sup>2</sup>,H<sub>a</sub>) in 4,6-dimethyl-1,3-dioxane 157.4 Hz [16] is equal to <sup>1</sup>J(C<sup>2</sup>,H) we have obtained for both isomers of compound **IV** confirming the equatorial orientation of the furyl substituent.

The opposite effect is observed with the coupling constants <sup>13</sup>C–<sup>1</sup>H at C<sup>5</sup>: <sup>1</sup>J(C<sup>5</sup>,H<sub>a</sub>) by 10.9 Hz is larger than <sup>1</sup>J(C<sup>5</sup>,H<sub>e</sub>) due to the hyperconjugation interaction σ(C–H<sub>e</sub>) → σ\*(C–O); this also permits the unambiguous establishment of the orientation of the vinyloxy group.

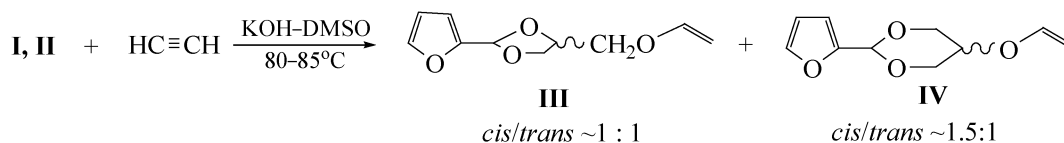
The data obtained show that in the prevailing *cis*-isomer of vinyl ether **IV** the substituents have the equatorial-axial orientation, and in the minor *trans*-isomer, diequatorial orientation.

This conclusion was also confirmed by the calculation

Scheme 1.



Scheme 2.



of the total energy for compound **IV** by the B3LYP/6-311G\*\*. According to the calculations the conformers with diequatorial and equatorial-axial orientation have close energies (1 kcal mol<sup>-1</sup>) and by 2–3 kcal mol<sup>-1</sup> they are more energy feasible than the corresponding inversion conformers.

The furan ring in both isomers of 4-vinyloxymethyl-2-(2-furyl)-1,3-dioxolane (**III**) takes the pseudoequatorial position.

The fragmentation character of the synthesized compounds under the electron impact (70 eV) provides a possibility to identify their structure from the mass spectra. The primary fragmentation act of isomers of vinyl ether **III** is due to the elimination of CH<sub>2</sub>OCH=CH<sub>2</sub> radical with the formation of the ion with *m/z* 139, whose further decomposition with the ejection of the propionaldehyde molecule leads to the ion with *m/z* 81 having the maximum abundance. The peak of the maximum intensity in the mass spectrum of 5-vinyloxy-2-(2-furyl)-1,3-dioxane is an odd-electron ion of *m/z* 42 which probably forms by the elimination of the acetaldehyde molecule and methyl radical from the ion with *m/z* 101. The latter can form by the elimination of the furoyl radical (*m/z* 95) from the molecular ion. In the mass spectra of vinyl ethers **III** and **IV** peaks of low intensity [*M*]<sup>+</sup> (*I*<sub>rel</sub> 1–2%) are present. The absence of peaks of *m/z* 129 in the spectra of both 4-vinyloxymethyl-2-(2-furyl)-1,3-dioxolane and 5-vinyloxy-2-(2-furyl)-1,3-dioxane shows that the elimination of the furyl radical characteristic of 2-substituted 1,3-dioxolane and 1,3-dioxane [17] is less favorable in these compounds.

Hence by the performed study an efficient preparation method was developed for new vinyl ethers with furan and cycloacetal fragments. This result was achieved owing to the application for the activation of the nucleophilic addition of hydroxy-1,3-dioxacyclanes to acetylene of the superbasic catalytic system KOH–DMSO. The obtained functionalized vinyl ethers are promising monomers and initial compounds for the synthesis of new furan derivatives.

## EXPERIMENTAL

NMR spectra were registered at room temperature on a spectrometer Bruker DPX-400 [400.13 (<sup>1</sup>H), 100.62 MHz (<sup>13</sup>C)] in CDCl<sub>3</sub> solutions. The assignment of signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra was carried out with the use of 2D correlation methods COSY, NOESY, HSQC, and

HMBC. The δ values were measured from the residual signals of the deuterated solvent. IR spectra were recorded on a spectrophotometer Bruker JFS-25 in the range 400–4000 cm<sup>-1</sup> in thin films. Mass spectrum was measured on an instrument Shimadzu GCMS-QP5050A (capillary column SPB-5, 60 000 mm × 0.25 mm × 0.25 μm), injector temperature 250°C, carrier gas helium, flow rate 0.7 ml min, pressure 250–300 kPa, flow division 1 : 12; ramp from 60 to 250°C at a rate 10 deg/min. Quadrupole mass-analyzer, electron impact, 70 eV, ion source at 250°C; range of detected masses 39–400 Dalton.

Furfural and glycerol just before use were purified by fractional distillation, the other reagents and solvents were used without additional purification.

Initial hydroxy-1,3-dioxacyclanes **I** and **II** were prepared by procedure [9] in 76% yield, bp 130–132°C (5 mm Hg), *n*<sub>D</sub><sup>20</sup> 1.5015 {bp 150–157°C (9 mm Hg), *n*<sub>D</sub><sup>20</sup> 1.5037 [9]}. The spectral characteristics of compounds obtained were identical to those described in [9]. The isomer ratio *cis*-(**I**)–*trans*-(**I**)–*cis*-(**II**)–*trans*-(**II**) 26:26:29:19 was evaluated from integral intensity of acetal protons H<sup>2</sup> in the <sup>1</sup>H NMR spectrum. The protons appearing as singlets of equal intensity correspond to *cis*- (5.88 ppm) and *trans*-5-hydroxymethyl-2-(2-furyl)-1,3-dioxolane (6.02 ppm). The signals of analogous protons of 5-hydroxy-2-(2-furyl)-1,3-dioxane (**II**) are shifted upfield (δ 5.58 and 5.47 ppm) and show the prevalence of the *cis*-isomer (~1.5 : 1).

**Vinyl ethers of hydroxy-1,3-dioxacyclanes III and IV.** *a.* Into a reaction flask of 50 ml capacity equipped with an efficient reflux condenser, a thermometer, magnetic stirrer, and a bubbler for acetylene input was charged 25 ml of DMSO, 4.25 g (25 mmol) of the mixture of hydroxy-1,3-dioxacyclanes **I** and **II**, 0.82 g (12.5 mmol) of KOH · 0.5H<sub>2</sub>O, the mixture was heated at 80–85°C, and acetylene was passed at a rate ~1 l/h till the disappearance of the signals of initial compounds in the <sup>13</sup>C NMR spectrum of the reaction mixture (3 h). On the completion of the synthesis the reaction mixture was diluted with water (1 : 1), the reaction products were extracted into ethyl ether (7 × 15 ml), the combined extracts were washed with water (2 × 10 ml) and dried with Na<sub>2</sub>SO<sub>4</sub>. On removing the solvent the crude product was of the purity >95%. The vacuum distillation afforded 4.40 g (90%) of the mixture of target vinyl ethers **III** and **IV**.

*b.* In a pressure reactor (0.25 l) a mixture of 8.50 g (50 mmol) of compounds **I** and **II**, 1.65 g (25 mmol) of KOH · 0.5H<sub>2</sub>O, and 50 ml DMSO in the presence

of acetylene (initial pressure 14 at). The workup of the reaction mixture was similar to that in procedure *a*. After the vacuum distillation 8.62 g (88%) of the mixture of vinyl ethers **III** and **IV** was obtained. Colorless liquid, bp 124–126°C (8 mm Hg),  $n_D^{20}$  1.4947. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3149 m, 3120 m, 3045 w ( $\text{CH}_2=$ ,  $\text{CH}=\text{}$ , Fur), 2979 s, 2923 s, 2880 s ( $\text{CH}_2$ ), 2767 w (cycloacetals), 1639 s, 1621 s ( $\text{C}=\text{C}$ ), 1505 m (Fur), 1471 m, 1456 m, 1414 m ( $\text{CH}_2$ ), 1376 m, 1361 m, 1324 s ( $\text{CH}_2=$ ,  $\text{CH}=\text{}$ , Fur), 1271 m (Fur), 1243 sh, 1200 s, 1154 s, 1093 s, 1058 sh, 1029 s (cycloacetals, COC,  $\text{C}=\text{C}$ ), 1011 s, 983 s (Fur), 966 s, 940 m, 924 s, 884 m, 867 m, 823 s ( $\text{CH}_2=$ ,  $\text{CH}=\text{}$ , Fur), 747 s, 599 m, 534 w, 505 w (Fur). Found, %: C 60.92; H 5.94.  $\text{C}_{10}\text{H}_{12}\text{O}_4$ . Calculated, %: C 61.22; H 6.16.

**cis-4-Vinyloxymethyl-2-(2-furyl)-1,3-dioxolane (III).**  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.78 and 3.87 (1H each,  $\text{OCH}_2$ ), 3.99 (1H,  $\text{H}^5$ ), 4.09 (2H,  $\text{H}^5$ ,  $=\text{CH}_{\text{cis}}$ ), 4.22 (1H,  $=\text{CH}_{\text{trans}}$ ), 4.42 (1H,  $\text{H}^4$ ), 5.90 (1H,  $\text{H}^2$ ), 6.34 (1H,  $\text{H}^4_{\text{Fur}}$ ), 6.47 (1H,  $=\text{CHO}$ ), 6.48 (1H,  $\text{H}^3_{\text{Fur}}$ ), 7.42 (1H,  $\text{H}^5_{\text{Fur}}$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 67.63 ( $\text{C}^5$ ), 67.92 ( $\text{OCH}_2$ ), 74.40 ( $\text{C}^4$ ), 87.14 ( $\text{CH}_2=$ ), 98.29 ( $\text{C}^2$ ), 109.34 ( $\text{C}^3_{\text{Fur}}$ ), 110.20 ( $\text{C}^4_{\text{Fur}}$ ), 143.30 ( $\text{C}^5_{\text{Fur}}$ ), 150.24 ( $\text{C}^2_{\text{Fur}}$ ), 151.37 ( $\text{OCH}=\text{}$ ). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 196 (1) [ $M$ ] $^{+}$ , 152 (3), 139 (7), 97 (13), 96 (10), 95 (47), 94 (25), 81 (100), 69 (15), 68 (12), 57 (32), 55 (30), 53 (15), 52 (33), 51 (20), 45 (10), 44 (20), 43 (47), 42 (27).

**trans-4-Vinyloxymethyl-2-(2-furyl)-1,3-dioxolane (III).**  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.78 and 3.82 (1H each,  $\text{OCH}_2$ ), 3.87 (1H,  $\text{H}^5$ ), 4.04 (1H,  $=\text{CH}_{\text{cis}}$ ), 4.23 (2H,  $=\text{CH}_{\text{trans}}$ ,  $\text{H}^5$ ), 4.53 (1H,  $\text{H}^4$ ), 6.03 (1H,  $\text{H}^2$ ), 6.34 (1H,  $\text{H}^4_{\text{Fur}}$ ), 6.43 (1H,  $\text{H}^3_{\text{Fur}}$ ), 6.49 (1H,  $=\text{CHO}$ ), 7.41 (1H,  $\text{H}^5_{\text{Fur}}$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 67.07 ( $\text{C}^5$ ), 67.64 ( $\text{OCH}_2$ ), 74.03 ( $\text{C}^4$ ), 87.11 ( $\text{CH}_2=$ ), 98.05 ( $\text{C}^2$ ), 108.84 ( $\text{C}^3_{\text{Fur}}$ ), 110.12 ( $\text{C}^4_{\text{Fur}}$ ), 143.15 ( $\text{C}^5_{\text{Fur}}$ ), 150.81 ( $\text{C}^2_{\text{Fur}}$ ), 151.43 ( $\text{OCH}=\text{}$ ). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 196 (1) [ $M$ ] $^{+}$ , 152 (4), 139 (7), 97 (14), 96 (9), 95 (50), 94 (19), 81 (100), 69 (12), 68 (11), 57 (28), 55 (28), 53 (12), 52 (28), 51 (18), 45 (12), 44 (13), 43 (39), 42 (26).

**cis-5-Vinyloxy-2-(2-furyl)-1,3-dioxane (IV).**  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.81 (1H,  $\text{H}^5$ ), 4.06 (2H,  $\text{H}^{4a,6a}$ ), 4.13 (1H,  $=\text{CH}_{\text{cis}}$ ), 4.23 (1H,  $=\text{CH}_{\text{trans}}$ ), 4.33 (2H,  $\text{H}^{4e,6e}$ ), 5.62 (1H,  $\text{H}^2$ ), 6.36 (1H,  $\text{H}^4_{\text{Fur}}$ ), 6.44 (1H,  $=\text{CHO}$ ), 6.49 (1H,  $\text{H}^3_{\text{Fur}}$ ), 7.38 s (1H,  $\text{H}^5_{\text{Fur}}$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 68.17 ( $\text{C}^{4,6}$ ), 68.58 ( $\text{C}^5$ ),  $^1J_{\text{C,H}}$  143.1 Hz), 88.61 ( $\text{CH}_2=$ ), 95.71 ( $\text{C}^2$ ,  $^1J_{\text{C,H}}$  160.4 Hz), 107.83 ( $\text{C}^3_{\text{Fur}}$ ), 110.22 ( $\text{C}^4_{\text{Fur}}$ ), 142.53 ( $\text{C}^5_{\text{Fur}}$ ), 149.66 ( $\text{OCH}=\text{}$ ), 150.24 ( $\text{C}^2_{\text{Fur}}$ ). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %):

196 (1) [ $M$ ] $^{+}$ , 152 (2), 97 (20), 96 (13), 95 (51), 94 (17), 81 (39), 70 (26), 69 (14), 68 (12), 57 (32), 55 (18), 53 (9), 52 (17), 51 (11), 45 (10), 44 (25), 43 (43), 42 (100).

**trans-5-Vinyloxy-2-(2-furyl)-1,3-dioxane (IV).**  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.64 (2H,  $\text{H}^{4a,6a}$ ), 4.10 (1H,  $=\text{CH}_{\text{cis}}$ ), 4.17 (1H,  $\text{H}^5$ ), 4.38 (2H,  $\text{H}^{4e,6e}$ ), 4.39 (1H,  $=\text{CH}_{\text{trans}}$ ), 5.49 (1H,  $\text{H}^2$ ), 6.30 (1H,  $=\text{CHO}$ ), 6.36 (1H,  $\text{H}^4_{\text{Fur}}$ ), 6.44 (1H,  $\text{H}^3_{\text{Fur}}$ ), 7.40 (1H,  $\text{H}^5_{\text{Fur}}$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 66.79 ( $\text{C}^5$ ,  $^1J_{\text{C,H}}$  154.0 Hz), 69.03 ( $\text{C}^{4,6}$ ), 89.50 ( $\text{CH}_2=$ ), 95.74 ( $\text{C}^2$ ,  $^1J_{\text{C,H}}$  162.4 Hz), 107.88 ( $\text{C}^3_{\text{Fur}}$ ), 110.24 ( $\text{C}^4_{\text{Fur}}$ ), 142.71 ( $\text{C}^5_{\text{Fur}}$ ), 149.71 ( $\text{OCH}=\text{}$ ), 149.82 ( $\text{C}^2_{\text{Fur}}$ ). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 196 (2) [ $M$ ] $^{+}$ , 153 (1), 97 (20), 96 (14), 95 (50), 94 (17), 81 (33), 70 (34), 69 (18), 68 (9), 57 (24), 55 (20), 53 (9), 52 (12), 51 (12), 45 (13), 44 (36), 43 (45), 42 (100).

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## REFERENCES

- Oparina, L.A., Vysotskaya, O.V., Stepanov, A.V., Gusarova, N.K., and Trofimov, B.A., *Zh. Org. Khim.*, 2009, vol. 45, p. 134.
- Zheng, Y., Chen, X., and Shen, Y., *Chem. Rev.*, 2008, vol. 108, p. 5253; Zhou, C.-H., Beltrami, J.N., Fan, Y.-X., and Lu, G.Q. *Chem. Soc. Rev.*, 2008, vol. 37, p. 527; Garcna, E., Laca, M., Pérez, E., Garrido, A., and Peinado, J., *Energy & Fuels*, 2008, vol. 22, p. 4274.
- Chheda, J.N., Huber, G.W., and Dumesic, A.J., *Angew. Chem., Int. Ed.*, 2007, vol. 46, p. 7164; Corma, A., Iborra, S., and Velty, A., *Chem. Rev.*, 2007, vol. 107, p. 2411; Chheda, J.N., Roman-Leshkov, Y., and Dumesic, J.A., *Green. Chem.*, 2007, vol. 9, p. 342.
- Harvey, C.M., US Patent 6165987, 2000; *Chem. Abstr.*, 1999, vol. 128, 196680; Shuster, D.E., Sawutz, D.G., and Varma, K.J., WO Patent 2004089355, 2004; Bell, A.R., Shephard, R.W., Iemma, S., and Stajic, V., WO Patent 2007062483, 2007; *Chem. Abstr.*, 2007, vol. 147, 58333.
- Rodier, J.-D. and Mahler, B., WO Patent 2005105149, 2005; *Chem. Abstr.*, 2006, vol. 143, 410646.
- Gandiny, A. and Belgacem, M.N., *Prod. Polym. Sci.*, 1997, vol. 22, p. 1201.
- Kottke, R.H., in *Kirk-Othmer Encyclopedia of Chemical Technology*, New York: Wiley & Sons, 1998, vol. 12, p. 259.
- Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C.A., Frederick, W.J., Jr., Hal-

- let, J.P., Leak, D.J., Liotta, C.L., Mielenz, J.R., Murphy, R., Templer, R., and Tschaplinski, T., *Science*, 2006, vol. 311, p. 484; Roman-Leshkov, Y., Barrett, C.J., Liu, Z.Y., and Dumesic, J.A., *Nature*, 2007, vol. 447, p. 982.
9. Gromachevskaya, E.V., Kvitkovskii, F.V., Usova, E.B., and Kul'nevich, V.G., *Khim. Geterotsikl. Soedin.*, 2004, p. 1137.
10. Zelikman, Z.I. and Kul'nevich, V.G., *Khim. Geterotsikl. Soedin.*, 1968, p. 367; Mel'nitskaya, G.A., Kuramshin, A.Kh., Khlebnikova, T.D., Mel'nitskii, I.A., and Kantor, E.A., *Zh. Strukt. Khim.*, 1997, vol. 38, p. 1083; Kantor, E.A., Khlebnikova, T.D., and Mel'nitskaya, G.A., RF Patent 2086550, 1997; *RF Byull. Izobr.*, 1997, no. 22; Li, Y., Zhang, X., Ren, T., and Zhou, J., *Synth. Commun.*, 2006, vol. 36, p. 1679.
11. Nen'ko, N.I., Kosulina, T.P., Kul'nevich, V.G., Smolyakov, V.P., Gonik, G.E., Pospelova, Yu.S., Knyr, L.L., Barchukova, A. Ya., Aleshin, E.P., and Galenko-Yaroshevskii, P.A., RF Patent 2042326, 1995; *RF Byull. Izobr.*, 1995, no. 24.
12. Khlebnikova, T.D., Kantor, E.A., and Tolmacheva, N.A., RF Patent 2141202, 1999; *RF Byull. Izobr.*, 1999, no. 32.
13. Shostakovskii, M.F., Atavin, A.S., Vasil'ev, N.P., Dubova, R.I., Dmitrieva, L.P., and Mikhaleva, A.I., *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1966, p. 1232.
14. Oparina, L.A., Vysotskaya, O.V., Parshina, L.N., Khil'ko, M. Ya., and Gusarova, N.K., *Zh. Org. Khim.*, 2008, vol. 44, p. 1458.
15. Bailey, W.F., Rivera, A.D., and Rossi, K., *Tetrahedron Lett.*, 1988, vol. 29, p. 5621.
16. Cuevas, G. and Juaristi, E., *J. Am. Chem. Soc.*, 2002, vol. 124, 13088.
17. Vul'fson, N.S., Zaikin, V.G., and Mikaya, A.I., *Mass-spektrometriya organicheskikh soedinenii* (Mass-Spectrometry of Organic Compounds), Moscow: Khimiya, 1986.