ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 9, pp. 1162–1167. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © L.A. Oparina, O.V. Vysotskaya, A.V. Stepanov, N.K. Gusarova, B.A. Trofimov, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 9, pp. 1166–1171.

Chemo- and Regioselective Reaction of Vinyl Furfuryl Ethers with Alcohols

L. A. Oparina, O. V. Vysotskaya, A. V. Stepanov, N. K. Gusarova, and B. A. Trofimov

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: boris_trofimov@irioch.irk.ru

Received March 27, 2012

Abstract—Furfuryl and tetrahydrofurfuryl vinyl ethers reacted with various alcohols under mild conditions (20–25°C, 1–3 h, 1 wt % of CF_3COOH) with high chemo- and regioselectivity to give the corresponding Markovnikov adducts at the vinyl group in up to 93% yield.

DOI: 10.1134/S1070428012090023

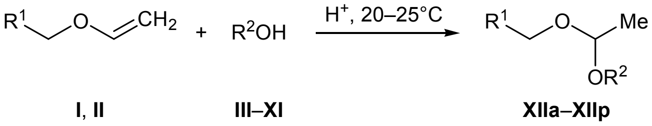
Persistent exhaust of natural gas and oil resources increases the role of renewable sources of organic materials [1–3], primarily of plant biomass. For example, furfural and furfuryl alcohol that are readily obtainable from natural oligo- and polysaccharides, have received growing application in organic synthesis [1, 4–7]. Large-scale solvents [8, 9], fuel additives [10, 11], and biodegradable polymers [12] have already been created on the basis of furfural. Furfuryl alcohol is a starting material in large-scale syntheses of furan resins [13], adhesives, and paints [14]. Tetrahydrofurfuryl alcohol is used as nontoxic (“green”) solvent in the manufacture of acrylates and epoxy resins, as well as in the preparation of plasticizers like tetrahydrofurfuryl oleate [1].

Vinyl ethers derived from alcohols of the furan series have become accessible due to development of a convenient and efficient procedure for their synthesis by vinylation of furfuryl and tetrahydrofurfuryl alcohols with acetylene under atmospheric pressure in the presence of special superbasic catalytic systems [15, 16]. They are now regarded as base building blocks for the preparation of new furan derivatives, i.e., they can be used as “anchor carriers” of furan functionality [17, 18]. A promising line in the synthetic application of vinyl ethers of the furan series is their reaction with alcohols. It was shown previously that alkanols and allyl and propargyl alcohols in the presence of hydrochloric [19–21] or *p*-toluenesulfonic acid [22] add at the double bond of furfuryl vinyl ether **I** to produce the corresponding Markovnikov adducts, alkyl furfuryl acetals, in 20–40% yield. The low yield is likely to be related to facile disproportionation of the resulting acetals, leading to symmetric dialkyl and difurfuryl acetals. It was also reported that furan ring undergoes acid-catalyzed cleavage with formation of 1,4-dicarbonyl compounds [23–26]. The reactions of tetrahydrofurfuryl vinyl ether with allyl and propargyl alcohols in the presence of a catalytic amount of hydrochloric acid were more selective, and the resulting mixed acetals (yield up to 70%) were more resistant to symmetrization [21]. 2-{[1-(Furan-2-ylmethoxy)ethoxy]methyl}furan and 2-{[1-(2-methoxyethoxy)ethoxy]methyl}furan obtained from vinyl ether **I** and furfuryl alcohol or 2-methoxyethanol under acidic conditions were used as effective dopes to electrolyte in lithium–sulfur batteries [15].

The goal of the present study was to develop a convenient and efficient procedure for the synthesis of acetals containing furan and tetrahydrofuran rings via chemo- and regioselective addition of various alcohols at the double bond of furfuryl vinyl ether [**I**, 2-(vinyloxymethyl)furan] and tetrahydrofurfuryl vinyl ether [**II**, 2-(vinyloxymethyl)tetrahydrofuran] under acidic conditions.

We found that 2-(vinyloxymethyl)furan (**I**) and 2-(vinyloxymethyl)tetrahydrofuran (**II**) reacted with various alcohols [saturated alcohols **III**–**VI**, unsaturated alcohols **VII** and **VIII**, fluorinated alcohol **IX**, 2-methoxyethanol (**X**), and furfuryl alcohol (**XI**)] in the presence of a catalytic amount of trifluoroacetic acid (1 wt %) to produce acetals **XIIa**–**XIIp** with high

Scheme 1.



I, R^1 = furan-2-yl; **II**, R^1 = tetrahydrofuran-2-yl; **III**, R^2 = Me; **IV**, R^2 = Et; **V**, R^2 = *i*-Pr; **VI**, R^2 = *t*-Bu; **VII**, R^2 = CH_2=$CHCH_2$; **VIII**, R^2 = $CH{\equiv}CCH_2$; **IX**, R^2 = $CHF_2CF_2CH_2$; **X**, R^2 = $MeOCH_2CH_2$; **XI**, R^2 = furan-2-ylmethyl.

chemo- and regioselectivity (Scheme 1). The reactions were complete in 1–3 h at room temperature (see table). No products of furan ring opening, which might be expected under acidic conditions [23–26], were detected in the reaction mixtures.

The progress of reactions was monitored by IR and ^{1}H NMR spectroscopy. In the IR spectra of the reaction mixtures we observed gradual disappearance of absorption bands typical of vinyloxy (3030, 1640–1618, 1320, 1200, 960, 817 cm^{-1}) and hydroxy groups (3450 cm^{-1}), and spectral pattern in the region of C–O–C absorption (1050–1205 cm^{-1}) changed. The ^{1}H NMR spectra contained signals characteristic of furfuryl and alkoxy groups, and signals from the OCHO proton (δ 4.6–4.9 ppm, q) and methyl group (δ ~1.3 ppm, d) appeared.

When the reaction was complete, calcined potassium carbonate was added to the reaction mixture to neutralize the catalyst, and the mixture was kept for 0.5–1 h and filtered. Neutralization of the catalyst was also achieved in a different way, by passing the mixture through a thin layer of basic alumina and subsequent washing of the sorbent with diethyl ether.

The proposed conditions (room temperature and the use of trifluoroacetic acid instead of aggressive *p*-toluenesulfonic or hydrochloric acid) made it possible to largely avoid disproportionation of unsymmetrical acetals **XII**. The stability of acetals **XII** to disproportionation depended on the nature of the R^2 group in the alcohol fragment. Acetals **XIIe**–**XIIg** and **XIIn**–**XIIp** having electron-withdrawing organyloxy groups almost did not undergo disproportionation during their synthesis and subsequent distillation (after neutralization of the catalyst), and they were isolated in fairly high yields 82–93% (see table). Alkoxy acetals **XIIa**–**XIId**, **XIIh**, and **XIIj**–**XIIm** were isolated in a lower yield (61–74%) due to greater contribution of disproportionation leading to the corresponding symmetrical acetals.

Reaction of furfuryl vinyl ethers **I** and **II** with alcohols **III**–**XI**

Reactants	Reaction time, h	Product (yield, %)
I + **III**	3	**XIIa** (68)
I + **IV**	3	**XIIb** (64)
I + **V**	2	**XIIc** (65)
I + **VI**	3	**XIId** (68)
I + **VII**	2	**XIIe** (82)
I + **VIII**	2	**XIIf** (93)
I + **IX**	2	**XIIg** (87)
I + **X**	2	**XIIh** (74)
I + **XI**	2	**XIIi** (92)
II + **III**	1.5	**XIIj** (62)
II + **IV**	1.5	**XIIk** (61)
II + **V**	1.5	**XIIl** (70)
II + **VI**	1.5	**XIIm** (74)
II + **VII**	1	**XIIn** (86)
II + **VIII**	1	**XIIo** (83)
II + **IX**	1	**XIIp** (85)

The reactivities of vinyl ethers **I** and **II** were compared by the competing reaction technique. As model reactions we examined electrophilic addition of allyl alcohol (**VII**) and prop-2-yn-1-yl alcohol (**VIII**) to the above substrates, the molar ratio **I**–**II**–**VII** (**VIII**) being 1 : 1 : 1 (room temperature, 3 h, 1 wt % of CF_3COOH). The ratio of acetals **XIIe**/**XIIn** and **XIIf**/**XIIo** in the reaction mixture was estimated by the intensities of the OCHO signals in the ^{1}H NMR spectrum (δ 4.81/4.76 for **XIIe**/**XIIn** and 4.92/4.87 ppm for **XIIf**/**XIIo**). Unsaturated alcohols **VII** and **VIII** were selected taking into account that acetals **XII** derived therefrom are stable (no disproportionation occurred during their synthesis). It was found that the concentration of the adducts obtained from tetrahydrofurfuryl vinyl ether was greater by a factor of 2.2–2.4 than the concentration of the corresponding adducts derived from furfuryl vinyl ether, i.e., saturated ether **II** is more reactive than furan-containing ether **I**.

The choice of trifluoroacetic acid as catalyst for electrophilic addition of hydroxy compounds to furfuryl vinyl ethers was not fortuitous. It is known that perfluorinated carboxylic acids are specific and mild selective catalysts of electrophilic addition to vinyloxy group [27–29]. In fact, the reaction of vinyl ether **I** with *tert*-butyl alcohol in the presence of *p*-toluenesulfonic acid (1 wt %) was accompanied by considerable heat evolution, and the yield of acetal **XIId** was as poor as 12%. Under these conditions, appreciable amounts of symmetric acetals and tarry products were obtained; the latter could be formed as a result of cleavage of the furan ring.

The structure of acetals **XIIa**–**XIIp** was proved by IR and ^{1}H and ^{13}C NMR spectroscopy. The presence of a chiral center in molecules **XIIa**–**XIIi** makes protons in the OCH_2 group nonequivalent, and their signals appear in the ^{1}H NMR spectrum as two doublets with equal intensities at δ 4.60–4.70 ppm. Acetals **XIIj**–**XIIp** obtained from 2-(vinyloxymethyl)tetrahydrofuran were isolated as mixtures of two diastereoisomers. Signals from the C^3H_2 protons in the tetrahydrofuran ring and from the OCH_2 group were observed separately [δ, ppm: 1.9 and 1.5 (3-H), 3.5 and 3.3 (OCH_2)], and each signal, apart from geminal coupling constant ^{2}J, displayed additional couplings, so that complex multiplets were observed. In the ^{13}C NMR spectra of **XIIj**–**XIIp** double sets of signals from all carbon atoms in the tetrahydrofurfuryl and acetal fragments, as well as from the alkoxy carbon atom neighboring to the asymmetric center, were present. Acetals containing furan (**XIIa**–**XIIi**) and tetrahydrofuran rings (**XIIj**–**XIIp**) are readily soluble in most organic solvents and insoluble in water.

To conclude, by trifluoroacetic acid-catalyzed addition of alcohols to the vinyloxy group of furfuryl and tetrahydrofurfuryl vinyl ethers we have demonstrated the possibility of using them as anchor carriers of furan (tetrahydrofuran) functionality in the synthesis of furan-containing acetals.

EXPERIMENTAL

The NMR spectra were recorded from solutions in $CDCl_3$ at room temperature on a Bruker DPX-400 spectrometer operating at 400.13 (^{1}H) and 100.62 MHz (^{13}C). The IR spectra (400–4000 cm^{-1}) were measured from thin films on a Bruker JFS-25 spectrometer.

General procedure for the addition of alcohols to furfuryl vinyl ethers I and II. A catalytic amount (1 wt %) of trifluoroacetic acid was added to a mixture of 10 mmol of vinyl ether **I** or **II** and 10 mmol of alcohol **III**–**XI**, and the mixture was stirred for 1–3 h at room temperature on a magnetic stirrer. The progress of the reaction was monitored by IR spectroscopy. When the reaction was complete (absorption bands typical of vinyloxy and hydroxy groups disappeared completely from the IR spectrum of the reaction mixture), the mixture was neutralized by treatment with K_2CO_3 (~2–3 wt %, 0.5–1 h, room temperature), and acetals **XIIa**–**XIIp** were isolated by vacuum distillation.

2-[(1-Methoxyethoxy)methyl]furan (XIIa). Colorless liquid. Yield 1.06 g (68%), bp 60°C (8 mm), n_D^{20} = 1.4551; published data [21]: bp 50°C (3 mm), n_D^{20} = 1.4610. IR spectrum, ν, cm^{-1}: 3150, 3120, 2990, 2935, 2831, 1504, 1452, 1390, 1366, 1339, 1281, 1268, 1224, 1209, 1150, 1126, 1092, 1045, 1027, 1015, 989, 920, 897, 885, 867, 813, 743, 601. ^{1}H NMR spectrum, δ, ppm: 1.34 d (3H, Me, J = 5.4 Hz), 3.34 s (3H, OMe), 4.47 d and 4.55 d (1H each, OCH_2, J = 12.7 Hz), 4.76 q (1H, OCHO, J = 5.4 Hz), 6.32 s and 6.34 s (1H each, 3-H, 4-H), 7.41 s (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 18.99 (Me), 51.92 (OMe), 59.02 (CH_2), 99.53 (CH), 108.94 (C^4), 110.23 (C^3), 142.67 (C^5), 151.81 (C^2). Found, %: C 61.30; H 7.54. $C_8H_{12}O_3$. Calculated, %: C 61.51; H 7.74.

2-[(1-Ethoxyethoxy)methyl]furan (XIIb). Colorless liquid. Yield 1.09 g (64%), bp 45°C (1 mm), n_D^{20} = 1.4501; published data [21]: bp 54°C (1 mm), n_D^{20} = 1.4500. IR spectrum, ν, cm^{-1}: 3147, 3121, 2979, 2933, 2900, 2879, 1504, 1445, 1384, 1281, 1272, 1225, 1150, 1126, 1079, 1013, 989, 920, 897, 885, 867, 813, 787, 601. ^{1}H NMR spectrum, δ, ppm: 1.18 t (3H, Me, J = 7.1 Hz), 1.30 d (3H, Me, J = 5.4 Hz), 3.42 d.q and 3.57 d.q (1H each, OCH_2, J = 7.1, 11.8 Hz), 4.46 d and 4.55 d (1H each, OCH_2, J = 12.7 Hz), 4.78 q (1H, OCHO, J = 5.4 Hz), 6.32 s and 6.34 s (1H each, 3-H, 4-H), 7.40 s (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 15.33 (Me), 19.06 (Me), 58.66 and 59.12 (CH_2), 98.53 (CH), 108.84 (C^4), 110.09 (C^3), 142.47 (C^5), 151.46 (C^2). Found, %: C 63.91; H 8.42. $C_9H_{14}O_3$. Calculated, %: C 63.51; H 8.29.

2-[(1-Isopropoxyethoxy)methyl]furan (XIIc). Colorless liquid. Yield 1.20 g (65%), bp 58–60°C (4 mm), n_D^{20} = 1.4446. IR spectrum, ν, cm^{-1}: 3148, 3119, 2974, 2935, 2875, 1504, 1466, 1455, 1448, 1391, 1380, 1370, 1332, 1280, 1268, 1225, 1186, 1151, 1131, 1086, 1028, 1016, 989, 950, 920, 901, 886, 860, 812, 737, 600. ^{1}H NMR spectrum, δ, ppm: 1.10 d and 1.18 d (3H each, Me, J = 6.2 Hz), 1.39 d (3H, Me, J = 5.4 Hz), 3.87 d.q (1H, OCH, J = 6.2 Hz), 4.45 d and 4.49 d (1H each, OCH_2, J = 12.6 Hz), 4.83 q (1H, OCHO, J = 5.4 Hz), 6.24 d and 6.34 d.d (1H each, 3-H, 4-H, J = 3.2, 1.8 Hz), 7.34 d.d (1H, 5-H, J = 1.8, 1.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.14 (Me), 21.86 and 22.86 (Me), 57.70 (CH_2), 67.60 (CH), 97.00 (CH), 108.62 (C^4), 109.85 (C^3), 142.29 (C^5), 151.38 (C^2). Found, %: C 65.11; H 8.49. $C_{10}H_{16}O_3$. Calculated, %: C 65.19; H 8.75.

2-{[1-(*tert*-Butoxy)ethoxy]methyl}furan (XIId). Colorless liquid. Yield 1.35 g (68%), bp 62–64°C (4 mm), n_D^{20} = 1.4473. IR spectrum, ν, cm^{-1}: 3147, 3118, 2977, 2936, 2908, 2874, 1504, 1474, 1460, 1446, 1383, 1366, 1322, 1260, 1236, 1226, 1198, 1150, 1112, 1092, 1035, 1016, 991, 966, 920, 884, 839, 807, 736, 600. ^{1}H NMR spectrum, δ, ppm: 1.23 s (9H, *t*-Bu), 1.30 d (3H, Me, *J* = 5.2 Hz), 4.46 s (2H, OCH$_2$), 5.00 q (1H, OCHO, *J* = 5.2 Hz), 6.24 d and 6.34 d (1H each, 3-H, 4-H, *J* = 1.3 Hz), 7.34 s (1H, 5-H). ^{13}C NMR spectrum, δ$_C$, ppm: 21.16 (Me), 28.05 (C**Me**$_3$), 56.51 (CH$_2$), 73.30 (**C**Me$_3$), 92.94 (CH), 107.47 (C^4), 109.53 (C^3), 141.72 (C^5), 151.75 (C^2). Found, %: C 66.49; H 9.20. $C_{11}H_{18}O_3$. Calculated, %: C 66.64; H 9.15.

2-{[1-(Allyloxy)ethoxy]methyl}furan (XIIe). Colorless liquid. Yield 1.49 g (82%), bp 68°C (4 mm), n_D^{20} = 1.4705; published data [21]: bp 84°C (13 mm), n_D^{20} = 1.4647. IR spectrum, ν, cm^{-1}: 3148, 3120, 3082, 2989, 2937, 2869, 1647, 1504, 1458, 1447, 1391, 1367, 1337, 1268, 1253, 1150, 1125, 1097, 1030, 992, 920, 886, 812, 739, 600. ^{1}H NMR spectrum, δ, ppm: 1.38 d (3H, Me, *J* = 5.4 Hz), 4.04 m and 4.12 m (1H each, OCH$_2$), 4.51 d and 4.56 d (1H each, OCH$_2$, *J* = 12.7 Hz), 4.88 q (1H, OCHO, *J* = 5.4 Hz), 5.19 d.d (1H, CH$_2$=, *J* = 10.2, 1.2 Hz), 5.31 d.d (1H, CH$_2$=, *J* = 17.1, 1.2 Hz), 5.94 m (1H, CH=), 6.32 d and 6.35 d.d (1H each, 3-H, 4-H, *J* = 3.0, 1.6 Hz), 7.42 d.d (1H, 5-H, *J* = 1.6, 0.8 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 19.46 (Me), 58.71 (CH$_2$), 65.77 (CH$_2$), 98.37 (CH), 108.82 (C^4), 110.13 (C^3), 116.59 (CH$_2$=), 134.53 (CH=), 142.59 (C^5), 151.68 (C^2). Found, %: C 65.25; H 7.65. $C_{10}H_{14}O_3$. Calculated, %: C 65.91; H 7.74.

2-{[1-(Prop-2-yn-1-yloxy)ethoxy]methyl}furan (XIIf). Colorless liquid. Yield 1.67 g (93%), bp 95°C (5 mm), n_D^{20} = 1.4769; published data [21]: bp 74°C (3 mm), n_D^{20} = 1.4738. IR spectrum, ν, cm^{-1}: 3294, 3149, 3122, 2990, 2933, 2870, 2119, 1504, 1454, 1445, 1393, 1367, 1338, 1268, 1225, 1202, 1151, 1125, 1095, 1032, 1016, 987, 972, 920, 894, 886, 847, 815, 743, 673, 638, 600. ^{1}H NMR spectrum, δ, ppm: 1.36 d (3H, Me, *J* = 5.4 Hz), 2.41 t (1H, CH≡, *J* = 2.4 Hz), 4.21 t (2H, OCH$_2$, *J* = 2.4 Hz), 4.50 d and 4.55 d (1H each, OCH$_2$, *J* = 12.6 Hz), 4.95 q (1H, OCHO, *J* = 5.4 Hz), 6.31 m (2H, 3-H, 4-H), 7.38 br.s (1H, 5-H). ^{13}C NMR spectrum, δ$_C$, ppm: 19.55 (Me), 52.60 and 59.16 (OCH$_2$), 74.03 (CH≡), 79.94 (C≡), 98.28 (CH), 109.19 (C^4), 110.34 (C^3), 142.88 (C^5), 151.60 (C^2). Found, %: C 66.50; H 6.66. $C_{10}H_{12}O_3$. Calculated, %: C 66.65; H 6.71.

2-{[1-(2,2,3,3-Tetrafluoropropoxy)ethoxy]methyl}furan (XIIg). Colorless liquid. Yield 2.23 g (87%), bp 85°C (3 mm), n_D^{20} = 1.4122. IR spectrum, ν, cm^{-1}: 3153, 3125, 2995, 2942, 2893, 1504, 1461, 1446, 1391, 1369, 1341, 1279, 1231, 1206, 1151, 1121, 1103, 1030, 1016, 968, 941, 921, 910, 886, 835, 818, 743, 711, 691, 601, 547. ^{1}H NMR spectrum, δ, ppm: 1.37 d (3H, Me, *J* = 5.3 Hz), 3.89 m (2H, CH$_2$), 4.50 d and 4.58 d (1H each, OCH$_2$, *J* = 12.7 Hz), 4.93 q (1H, OCHO, *J* = 5.3 Hz), 5.94 t.t (1H, CH$_2$F, *J* = 54.0, 4.9 Hz), 6.34 s and 6.35 s (1H each, 3-H, 4-H), 7.42 br.s (1H, 5-H). ^{13}C NMR spectrum, δ$_C$, ppm: 18.59 (Me), 59.27 (OCH$_2$), 61.01 t (**C**H$_2$CF$_2$, *J* = 28.7 Hz), 98.74 (CH), 109.31 t.t (HCF$_2$, *J* = 248.8, 34.6 Hz), 110.00 (C^4), 111.38 (C^3), 115.26 t.t (CF$_2$, *J* = 248.8, 26.5 Hz), 142.69 (C^5), 150.68 (C^2). Found, %: C 46.52; H 4.51; F 29.60. $C_{10}H_{12}F_4O_3$. Calculated, %: C 46.88; H 4.72; F 29.66.

2-{[1-(2-Methoxyethoxy)ethoxy]methyl}furan (XIIh). Colorless liquid. Yield 1.48 g (74%), bp 82–84°C (2 mm), n_D^{20} = 1.4582. IR spectrum, ν, cm^{-1}: 3148, 3118, 2987, 2930, 2879, 2827, 1504, 1454, 1387, 1369, 1340, 1282, 1244, 1225, 1200, 1150, 1124, 1100, 1067, 1015, 991, 971, 949, 920, 885, 853, 815, 750, 601. ^{1}H NMR spectrum, δ, ppm: 1.30 d (3H, Me, *J* = 5.2 Hz), 3.33 s (3H, OMe), 3.49 t (2H, OCH$_2$, *J* = 4.8 Hz), 3.54–3.59 m and 3.64–3.70 m (1H each, OCH$_2$), 4.46 d and 4.51 d (1H each, CH$_2$O, *J* = 12.8 Hz), 4.81 q (1H, OCHO, *J* = 5.2 Hz), 6.27 m (2H, 3-H, 4-H), 7.35 d (1H, 5-H, *J* = 0.8 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 18.59 (Me), 58.88 (OMe); 60.60, 66.40, 70.92 (OCH$_2$); 98.72 (CH), 109.21 (C^4), 110.26 (C^3), 142.57 (C^5), 151.79 (C^2). Found, %: C 60.06; H 8.11. $C_{10}H_{16}O_4$. Calculated, %: C 59.98; H 8.05.

2-{[1-(2-Furylmethoxy)ethoxy]methyl}furan (XIIi). Colorless liquid. Yield 2.04 g (92%), bp 112°C (2 mm), n_D^{20} = 1.4910; published data [20]: bp 126°C (4 mm), n_D^{20} = 1.4929. IR spectrum, ν, cm^{-1}: 3145, 3116, 2992, 2935, 2871, 1503, 1446, 1394, 1372, 1338, 1280, 1270, 1220, 1150, 1133, 1090, 1010, 969, 913, 810, 735, 600. ^{1}H NMR spectrum, δ, ppm: 1.33 d (3H, Me, *J* = 5.2 Hz), 4.48 d and 4.54 d (2H each, CH$_2$O, *J* = 12.8 Hz), 4.88 q (1H, OCHO, *J* = 5.2 Hz), 6.29 m (4H, 3-H, 4-H), 7.36 d (2H, 5-H, *J* = 0.8 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 15.23 (Me), 58.80 (CH$_2$), 98.95 (CH), 109.08 (C^4), 110.28 (C^3), 141.27 (C^5), 150.26 (C^2). Found, %: C 64.73; H 6.30. $C_{12}H_{14}O_4$. Calculated, %: C 64.85; H 6.35.

2-[(1-Methoxyethoxy)methyl]tetrahydrofuran (XIIj). Colorless liquid. Yield 0.99 g (62%), bp 98–

100°C (20 mm), n_D^{20} = 1.4411. IR spectrum, ν, cm^{-1}: 2976, 2932, 2872, 1459, 1445, 1381, 1339, 1284, 1273, 1135, 1089, 1052, 994, 919, 891, 838, 818, 700, 537. ^{1}H NMR spectrum, δ, ppm: 1.18 d and 1.19 d (3H, Me, *J* = 5.3 Hz), 1.50 m (1H, 3-H), 1.76 m (2H, 4-H), 1.82 m (1H, 3-H), 3.30 s (3H, OMe), 3.35 m and 3.44 m (1H each, OCH$_2$), 3.64 m and 3.70 m (1H each, 5-H), 3.91 m (1H, 2-H), 4.57 q (1H, OCHO, *J* = 5.3 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 18.62 (Me), 25.12 and 25.22 (C^4), 27.78 (C^3), 51.73 and 51.90 (OMe), 66.77 and 67.20 (OCH$_2$), 67.73 and 67.76 (C^5), 77.37 and 77.50 (C^2), 99.97 and 100.03 (OCHO). Found, %: C 59.62; H 10.27. $C_8H_{16}O_3$. Calculated, %: C 59.97; H 10.07.

2-[(1-Ethoxyethoxy)methyl]tetrahydrofuran (XIIk). Colorless liquid. Yield 1.06 g (61%), bp 54°C (4 mm), n_D^{20} = 1.4394. IR spectrum, ν, cm^{-1}: 2985, 2937, 2872, 2831, 1460, 1449, 1388, 1367, 1349, 1339, 1283, 1209, 1137, 1089, 1046, 994, 919, 891, 838, 818, 700, 537. ^{1}H NMR spectrum, δ, ppm: 1.18 t (3H, Me, *J* = 7.1 Hz), 1.28 d and 1.29 d (3H, Me, *J* = 5.3 Hz), 1.58 m (1H, 3-H), 1.84–1.90 m (3H, 3-H, 4-H), 3.42–3.65 m (4H, OCH$_2$), 3.71 m and 3.84 m (1H each, 5-H), 3.96 m (1H, 2-H), 4.94 q and 4.96 q (1H, OCHO, *J* = 5.3 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 15.33 (Me), 19.91 and 19.96 (Me), 25.69 and 25.76 (C^4), 28.00 and 28.09 (C^3), 60.60 and 64.96 (CH$_2$), 68.52 and 68.55 (C^5), 75.19 and 75.24 (C^2), 98.80 and 98.81 (OCHO). Found, %: C 61.81; H 10.19. $C_9H_{18}O_3$. Calculated, %: C 62.04; H 10.41.

2-[(1-Isopropoxyethoxy)methyl]tetrahydrofuran (XIIl). Colorless liquid. Yield 1.32 g (70%), bp 55°C (4 mm), n_D^{20} = 1.4379. IR spectrum, ν, cm^{-1}: 2973, 2934, 2872, 1464, 1380, 1371, 1330, 1284, 1186, 1135, 1085, 1050, 986, 951, 919, 897, 856, 823. ^{1}H NMR spectrum, δ, ppm: 1.08 d and 1.13 d (3H each, Me, *J* = 6.1 Hz), 1.24 d and 1.25 d (3H, Me, *J* = 5.3 Hz), 1.52–1.62 m (1H, 3-H), 1.79–1.94 m (3H, 3-H, 4-H), 1.40 m and 3.48 m (2H, OCH$_2$), 3.71 m (1H, 5-H), 3.80–3.86 m (2H, CH, 5-H), 3.96 m (1H, 2-H), 4.76 q and 4.77 q (1H, OCHO, *J* = 5.3 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 19.91 and 20.09 (Me); 21.59, 21.67, 22.73, and 22.78 (Me); 25.04 and 25.12 (C^4), 27.70 and 27.77 (C^3), 65.63 and 66.12 (CH$_2$), 67.40 (CH), 67.45 and 67.70 (C^5), 77.40 and 77.50 (C^2), 97.36 and 97.56 (OCHO). Found, %: C 64.01; H 10.39. $C_{10}H_{20}O_3$. Calculated, %: C 63.80; H 10.71.

2-{[1-(*tert*-Butoxy)ethoxy]methyl}tetrahydrofuran (XIIm). Colorless liquid. Yield 1.49 g (74%), bp 65°C (4 mm), n_D^{20} = 1.4376. IR spectrum, ν, cm^{-1}: 2976, 2935, 2873, 1473, 1461, 1390, 1381, 1365, 1334, 1260, 1236, 1200, 1132, 1091, 1051, 969, 951, 919, 897, 856, 823. ^{1}H NMR spectrum, δ, ppm: 1.21 s (9H, *t*-Bu), 1.25 d and 1.26 d (3H, Me, *J* = 5.3 Hz), 1.60 m (1H, 3-H), 1.84–1.90 m (3H, 3-H, 4-H), 3.45 m (2H, OCH$_2$), 3.73 m and 3.86 m (1H each, 5-H), 3.98 m (1H, 2-H), 4.92 q and 4.96 q (1H, OCHO, *J* = 5.3 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 22.16 and 22.24 (Me), 25.47 and 25.76 (C^4), 28.00 and 28.09 (C^3), 28.05 (C**Me**$_3$), 64.81 and 64.96 (CH$_2$), 67.55 and 67.80 (C^5), 73.28 (**C**Me$_3$), 75.40 and 75.50 (C^2), 96.84 and 96.91 (CH). Found, %: C 65.09; H 10.82. $C_{11}H_{22}O_3$. Calculated, %: C 65.31; H 10.96.

2-{[1-(Allyloxy)ethoxy]methyl}tetrahydrofuran (XIIn). Colorless liquid. Yield 1.60 g (86%), bp 62°C (3 mm), n_D^{20} = 1.4420; published data [21]: bp 82°C (4 mm), n_D^{20} = 1.4444. IR spectrum, ν, cm^{-1}: 3081, 2985, 2936, 2870, 1647, 1460, 1450, 1423, 1407, 1389, 1367, 1334, 1285, 1269, 1249, 1138, 1100, 1081, 1046, 993, 921, 902, 835. ^{1}H NMR spectrum, δ, ppm: 1.34 d and 1.35 d (3H, Me, *J* = 5.2 Hz), 1.55 m (1H, 3-H), 1.64 m (2H, 4-H), 1.83 m (1H, 3-H), 3.55–3.65 m (2H, OCH$_2$), 3.66 m and 3.81 m (1H each, 5-H), 4.01 d.d (1H, 2-H, *J* = 5.3, 13.1 Hz), 4.09 m and 4.16 m (1H each, OCH$_2$), 4.78 q and 4.80 q (1H, OCHO, *J* = 5.2 Hz), 5.13 d (1H, CH$_2$=, *J* = 10.4 Hz), 5.36 d (1H, CH$_2$=, *J* = 17.2 Hz), 5.96 m (1H, CH=). ^{13}C NMR spectrum, δ$_C$, ppm: 19.45 and 19.51 (Me), 25.46 and 25.55 (C^4), 28.05 and 28.11 (C^3); 65.98, 66.08, 66.42, and 66.84 (CH$_2$); 68.16 and 68.28 (C^5); 77.72 and 77.84 (C^2); 99.08 and 99.24 (CH); 116.42 (CH$_2$=), 134.67 (CH=). Found, %: C 64.94; H 9.40. $C_{10}H_{18}O_3$. Calculated, %: C 64.49; H 9.74.

2-{[1-(Prop-2-yn-1-yloxy)ethoxy]methyl}tetrahydrofuran (XIIo). Colorless liquid. Yield 1.53 g (83%), bp 80°C (4 mm), n_D^{20} = 1.4548; published data [21]: bp 95°C (2 mm), n_D^{20} = 1.4542. IR spectrum, ν, cm^{-1}: 2985, 2937, 2872, 2831, 1460, 1449, 1388, 1367, 1349, 1339, 1283, 1209, 1137, 1089, 1046, 994, 919, 891, 838, 818, 700, 537. ^{1}H NMR spectrum, δ, ppm: 1.29 d and 1.30 d (3H, Me, *J* = 5.4 Hz), 1.56 m (1H, 3-H), 1.84 m (2H, 4-H), 1.90 m (1H, 3-H), 2.37 m (1H, HC≡), 3.46 m and 3.53 m (1H each, OCH$_2$), 3.73 m and 3.82 m (1H each, 5-H), 3.99 m (1H, 2-H), 4.17 s (2H, OCH$_2$), 4.86 q and 4.87 q (1H, OCHO, *J* = 5.4 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 19.36 and 19.40 (Me), 25.51 and 25.63 (C^4), 28.01 and 28.11 (C^3), 52.54 and 52.67 (OCH$_2$), 67.04 and 67.49 (OCH$_2$), 68.17 and 68.23 (C^5), 73.84 (HC≡), 77.67 and 77.80 (C^2), 79.93 (C≡), 98.72 and 98.82 (OCHO), Found, %:

C 65.51; H 8.57. $C_{10}H_{16}O_3$. Calculated, %: C 65.19; H 8.75.

2-{[1-(2,2,3,3-Tetrafluoropropoxy)ethoxy]methyl}tetrahydrofuran (XIIp). Colorless liquid. Yield 2.21 g (85%), bp 80°C (3 mm), n_D^{20} = 1.3941. IR spectrum, ν, cm^{-1}: 2985, 2937, 2872, 2831, 1460, 1449, 1388, 1367, 1349, 1339, 1283, 1209, 1137, 1089, 1046, 994, 919, 891, 838, 818, 700, 537. ^1H NMR spectrum, δ, ppm: 1.34 d (3H, Me, J = 5.2 Hz), 1.59 m (1H, 3-H), 1.91 m (2H, 4-H), 1.97 m (1H, 3-H), 3.44 m and 3.59 m (1H each, OCH_2), 3.76–3.89 m (4H, CH_2, 5-H), 4.03 m (1H, 2-H), 4.88 q and 4.87 q (1H, OCHO, J = 5.2 Hz), 5.91 t.t (1H, CHF_2, J = 53.3, 5.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19.02 and 19.40 (Me), 25.60 and 25.74 (C^4), 28.02 and 28.15 (C^3), 61.21 t and 61.29 t ($\mathbf{C}H_2CF_2$, J = 27.4 Hz), 67.26 and 68.87 (OCH_2), 68.33 and 68.37 (C^5), 77.64 and 77.79 (C^2), 100.08 and 100.14 (OCHO), 109.27 t.t (HCF_2, J = 249.2, 34.3 Hz), 115.26 t.t (CF_2, J = 249.2, 26.2 Hz). Found, %: C 46.41; H 6.08; F 29.12. $C_{10}H_{16}F_4O_3$. Calculated, %: C 46.15; H 6.20; F 29.20.

REFERENCES

1. Chheda, J.N., Huber, G.W., and Dumesic, J.A., *Angew. Chem., Int. Ed.*, 2007, vol. 46, p. 7164.
2. Kuznetsov, B.N., Kuznetsova, S.A., and Taraban'ko, V.E., *Ross. Khim. Zh.*, 2004, vol. 48, p. 4.
3. Skurlatov, Yu.I., Duka, G.G., and Miziti, A., *Vvedenie v ekologicheskuyu khimiyu* (Introduction to Ecological Chemistry), Moscow: Vysshaya Shkola, 1994, p. 399.
4. Roman-Leshkov, Yu., *Ph.D. Thesis*, Madison, Wisconsin, 2008.
5. Werpy, T. and Petersen, G., Top value added chemicals from biomass. Report no. TP-510-35523. National Renewable Energy Laboratory, Golden, CO, 2004, p. 1.
6. Dalinyebo Trading and Development 2006: Furfural market overview. *http://www.dalinyebo.co.za/old/duT/FurfuralMarket.htm*
7. Win, D.T., *Aust. J. Techn.*, 2005, vol. 8, p. 185.
8. Ponomarev, A.A., *Sintezy i reaktsii furanovykh veshchestv* (Syntheses and Reactions of Furan Derivatives), Saratov: Saratov. Univ., 1960, p. 238.
9. Huang, W., Li, H., Zhu, B., Feng, Y., Wang, S., and Zhang, S., *Ultrason. Sonochem.*, 2007, vol. 14, p. 67.
10. Huber, G.W., Chheda, J.N., Barrett, C.J., and Dumesic, J.A., *Science*, 2005, vol. 308, p. 1446.
11. Lacome, Th., Montagne, X., Delfort, B., and Paille, F., EU Patent no. 1188812, 2002; *Chem. Abstr.*, 2003, vol. 136, no. 250119.
12. Okada, M., Tachikawa, K., and Aoi, K., *J. Polym. Sci. A: Polym. Chem.*, 1997, vol. 35, p. 2729.
13. Gandini, A. and Belgacem, M.N., *Prog. Polym. Sci.*, 1997, vol. 22, p. 1203.
14. Kottke, R.H., *Kirk-Othmer Encyclopedia of Chemical Technology*, New York, Wiley, 1998, vol. 12, p. 259.
15. Oparina, L.A., Vysotskaya, O.V., Stepanov, A.V., Rodionova, I.V., Myachina, G.F., Gusarova, N.K., and Trofimov, B.A., *Russ. J. Org. Chem.*, 2008, vol. 44, p. 120.
16. Oparina, L.A., Vysotskaya, O.V., Stepanov, A.V., Gusarova, N.K., and Trofimov, B.A., *Russ. J. Org. Chem.*, 2009, vol. 45, p. 131; Trofimov, B.A., Gusarova, N.K., Oparina, L.A., Vysotskaya, O.V., and Stepanov, A.V., Russian Patent no. 2359965, 2009; *Byull. Izobret.*, 2009, no. 18.
17. Stepanov, A.V., *Cand. Sci. (Chem.) Dissertation*, Irkutsk, 2010.
18. Oparina, L.A., Malysheva, S.F., Gusarova, N.K., Vysotskaya, O.V., Stepanov, A.V., Belogorlova, N.A., Albanov, A.I., and Trofimov, B.A., *Synthesis*, 2009, no. 20, p. 3427.
19. Rychkova, A.G. and Keller, R.E., *Zh. Obshch. Khim.*, 1961, vol. 31, p. 1849.
20. Uvarova, N.I., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1962, p. 78.
21. Skvortsova, G.G., An, V.V., An, L.M., and Rinkus, G.A., *Khimiya Geterotsiklicheskikh Soedinenii. Kislorodsoderzhashchie geterotsikly. Sbornik nauchnykh trudov* (Chemistry of Heterocyclic Compounds. Oxygen-Containing Heterocycles. A Collection of Scientific Papers), Riga: Zinatne, 1970, vol. 2, p. 97; An, V.V., Skvortsova, G.G., An, L.M., and Romanova, L.M., *ibid.*, p. 104.
22. Bowers, W.S., Unnithan, G.C., Fukushima, Y.-I., Toda, J., and Sugiyama, T., *Pesticide Sci.*, 1995, vol. 43, p. 1.
23. Denisov, V.R., Shevchenko, Z.A., and Khlebova, G.N., *Zh. Org. Khim.*, 1984, vol. 20, p. 2530.
24. Lange, J.P., van de Graaf, W.D, and Haan, R.J., *ChemSusChem.*, 2009, vol. 2, p. 437.
25. Timokhin, B.V., Baranskii, V.A., and Eliseeva, G.D., *Usp. Khim.*, 1999, vol. 68, p. 80.
26. Khusnutdinov, R.P., Baiguzina, A.R., Smirnov, A.A., Mukminov, R.R., and Dzhemilev, U.M., *Zh. Prikl. Khim.*, 2007, vol. 80, p. 1658.
27. Nedolya, N.A. and Trofimov, B.A., *Zh. Org. Khim.*, 1985, vol. 21, p. 271.
28. Nedolya, N.A. and Trofimov, B.A., *Zh. Org. Khim.*, 1985, vol. 21, p. 750.
29. Gorelova, O.V., Oparina, L.A., Parshina, L.N., Gusarova, N.K., and Trofimov, B.A., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 1683.