ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 4, pp. 468–473. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © S.G. Zlotin, G.V. Kryshtal', G.M. Zhdankina, A.V. Ignatenko, Ya.V. Burgart, V.I. Saloutin, O.N. Chupakhin, 2010, published in Zhurnal Organicheskoi Khimii, 2010, Vol. 46, No. 4, pp. 479–483.

Synthesis of 2,6-Bis(fluoroalkyl)-2,6-dihydroxytetrahydro-2*H*-pyran-3,5-dicarboxylates from Aldehydes and Fluorinated β-Oxo Esters in the Presence of Ionic Liquid–K_2CO_3 as Catalytic System

S. G. Zlotin[a], G. V. Kryshtal'[a], G. M. Zhdankina[a], A. V. Ignatenko[a], Ya. V. Burgart[b], V. I. Saloutin[b], and O. N. Chupakhin[b]

[a] *Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Leninskii pr. 47, Moscow, 119991 Russia*
e-mail: zlotin@ioc.ac.ru

[b] *Postovskii Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi 20, Yekaterinburg, 620219 Russia*

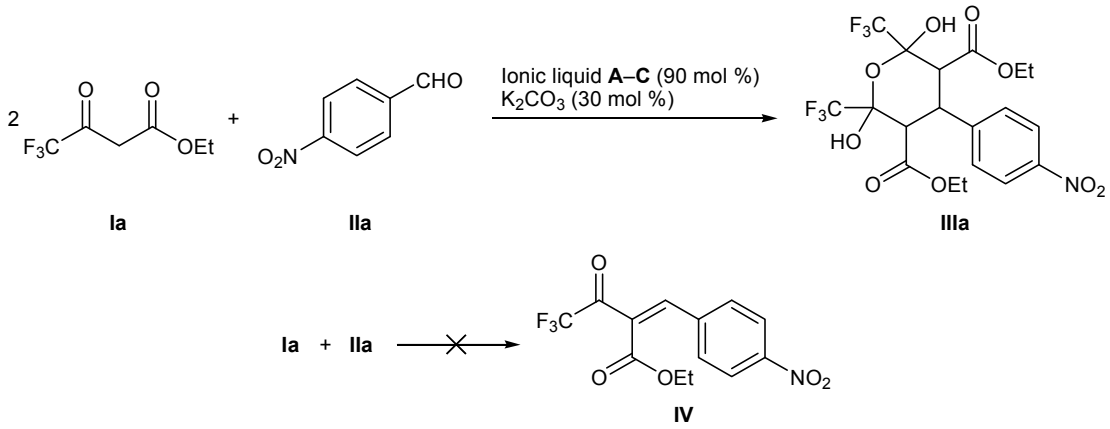
Received May 6, 2009

Abstract—An efficient procedure has been developed for the synthesis of 4-substituted 2,6-bis(fluoroalkyl)-2,6-dihydroxytetrahydro-2*H*-pyran-3,5-dicarboxylates by reactions of aldehydes with fluorine-containing β-oxo esters in heterogeneous catalytic system 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4]–K_2CO_3 activated by ultrasound. The system retains its catalytic activity for three reaction cycles.

DOI: 10.1134/S1070428010040020

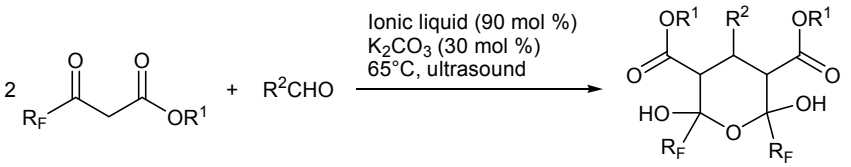
Base-catalyzed condensation of aldehydes with 1,3-dicarbonyl compounds (Knoevenagel reaction) is widely used to synthesize various polyfunctionalized organic compounds [1, 2]. These reactions are usually carried out in organic solvents (such as ethanol, tetrahydrofuran, benzene, or toluene) in the presence of base catalyst [3–12]. In the recent years, examples of Knoevenagel condensations performed in solutions in imidazolium salts with fluorine-containing anions [13–20] (i.e., ionic liquids [21–24]) were reported. The use of ionic liquids made it possible to shorten the reaction time and improve the yield [14, 17–20]. In addition, ionic liquids as solvents can be regenerated and used repeatedly. However, wide application of ionic liquids is limited due to their relatively high cost [25]. We have recently demonstrated that the amount of ionic liquid in Michael additions of nucleophiles to compounds possessing electron-deficient multiple

Scheme 1.



Ionic liquids: [bmim]BF_4 (**A**), [HexMim]NTf_2 (**B**), [BmPyr]NTf_2 (**C**).

Scheme 2.



I, R^1 = Et, R_F = CF_3 (**a**), $H(CF_2)_2$ (**c**), C_4F_9 (**e**); R^1 = Me, R_F = C_3F_7 (**b**), $H(CF_2)_4$ (**d**); **II**, R^2 = 4-$O_2NC_6H_4$ (**a**), Ph (**b**), 4-MeOCO-C_6H_4 (**c**), 4-ClC_6H_4 (**d**), 4-$MeOC_6H_4$ (**e**), 3-thienyl (**f**), pyridin-3-yl (**g**), Et (**h**); **III**, R_F = CF_3, R^1 = Et, R^2 = 4-$O_2NC_6H_4$ (**a**), Ph (**b**), 4-$MeOCOC_6H_4$ (**c**), 4-ClC_6H_4 (**d**), 4-$MeOC_6H_4$ (**e**), 3-thienyl (**f**), pyridin-3-yl (**g**), Et (**h**); R_F = C_3F_7, R^1 = Me, R^2 = 4-$O_2NC_6H_4$ (**i**), 4-ClC_6H_4 (**j**); R_F = $H(CF_2)_2$, R^1 = Et, R^2 = 4-$O_2NC_6H_4$ (**k**); R_F = $H(CF_2)_4$, R^1 = Me, R^2 = 4-$O_2NC_6H_4$ (**l**); R_F = C_4F_9, R^1 = Me, R^2 = 4-$O_2NC_6H_4$ (**m**).

bonds may be considerably reduced (to 30–90 mol %) by carrying out these reactions in the presence of a solid base [26, 27]. In such systems ionic liquid simultaneously acts as solvent (which reduces the viscosity of the reaction medium) and phase-transfer catalyst.

In the present work we were the first to perform reactions of aldehydes with fluorinated 1,3-dicarbonyl compounds in the system ionic liquid–solid base. The products, 4-substituted 2,6-bis(fluoroalkyl)-2,6-dihydroxytetrahydro-2*H*-pyran-3,5-dicarboxylates [28–31], attract interest as analogs of known compounds exhibiting antitumor activity [31]. We initially studied the condensation of ethyl 4,4,4-trifluoro-3-oxobutanoate (**Ia**) with 4-nitrobenzaldehyde (**IIa**) as model process. Compounds **Ia** and **IIa** reacted with each other in the presence of K_2CO_3 (30 mol %) and ionic liquid (30–90 mol %) to give tetrahydropyran derivative **IIIa** (Scheme 1), regardless of the reactant ratio. Even traces of 1:1 condensation product **IV** were not detected (compound **IV** was formed in nonpolar organic solvent, such as benzene or toluene) [29]. The best yield of **IIIa** was obtained when the reaction was carried out at 65°C under ultrasonic activation using 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] (**A**, 90 mol %; see table, run no. 3). Presumably, ultrasound increases dispersity of the solid base thus enhancing phase transfer of the reactants and product. The reaction rate and the yield of compound **IIIa** were lower in the absence of ultrasound, as well as in the presence of a smaller amount of ionic liquid (0–30 mol %; see table, run nos. 1, 2, 4). The yield also decreased upon lowering the temperature to 40°C (see table, run no. 5).

The described reaction also occurred in the presence of other ionic liquids (90 mol %), including 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [HexMim][NTf_2] (**B**) and 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [BmPyr][NTf_2] (**C**), but in these cases complete con-

Condensation of ethyl 3,3,3-trifluoro-3-oxobutanoate (**Ia**) with 4-nitrobenzaldehyde (**IIa**) in heterogeneous systems ionic liquid–K_2CO_3

Run no.	Iionic liquid (mol %)	Reaction time, h (65°C)	Ultrasound	Yield of **IIIa**, % (number of cycles)
1	–	7	+	40
2	**A** (30)	7	+	58
3	**A** (90)	7	+	81 (1), 80 (2), 80 (3)[a]
4[b]	**A** (90)	12	–	60
5[c]	**A** (90)	35	+	58[d]
6	**B** (90)	15	+	80
7	**C** (90)	22	+	78 (1), 82 (2), 82 (3)[a]

[a] A fresh portion of K_2CO_3 (30 mol %) was added.
[b] The reactin mixture was stirred using a magnetic stirrer.
[c] The reaction was carried out at 40°C; reactant ratio **Ia**–**IIa** 1:1.
[d] Calculated on the reacted compound **IIa**.

version of the initial reactants was achieved in a longer time, 15 and 22 h, respectively, against 7 h in the reaction with [bmim][BF_4] (**A**).

Taking into account that the catalytic system [bmim][BF_4] (90 mol %)–K_2CO_3 (30 mol %) ensured the best results in the condensation of ethyl 4,4,4-trifluoro-3-oxobutanoate (**Ia**) with 4-nitrobenzaldehyde (**IIa**), it was used to synthesize other 4-substituted 2,6-bis(fluoroalkyl)-2,6-dihydroxytetrahydro-2*H*-pyran-3,5-dicarboxylates **IIIb**–**IIIm**. Under these conditions we performed condensations of fluorinated β-oxo esters **Ia**–**Ie** having different polyfluoroalkyl groups with a series of aldehydes **IIa**–**IIh**, including aromatic aldehydes with electron-donating and electron-withdrawing substituents in the aromatic ring, aldehydes of the thiophene (**IIf**) and pyridine series (**IIg**), and propanal (**IIh**) (Scheme 2).

In all cases, the corresponding condensation products **IIIa**–**IIIm** were isolated in fairly high yields (71–88%), and the yields of previously reported compounds **IIIb** [28, 29], **IIIe** [28], **IIIg** [31], and **IIIh** [28] considerably exceeded those obtained in organic solvents. The catalytic system ionic liquid–K_2CO_3 is advantageous due to its easy regeneration. When the reaction was complete, compounds **III** were extracted into an organic solvent (benzene or diethyl ether), new portions of the reactants were added to the remaining mixture of ionic liquid and base, and the second reaction cycle was characterized by the same efficiency. The yield of the product was somewhat lower in the third cycle, but in increased again when an additional amount of the base was added to the system (see table, run nos. 3, 7).

Thus we have proposed a procedure for the synthesis of 4-substituted 2,6-bis(fluoroalkyl)-2,6-dihydroxytetrahydro-2*H*-pyran-3,5-dicarboxylates from the corresponding aldehydes and fluorinated β-keto esters in heterogeneous catalytic system ionic liquid–K_2CO_3, which conforms to "green chemistry" requirements. The proposed procedure is advantageous due to high yields of the target products, experimental simplicity, and minimal consumption of ionic liquid, and no organic solvent is necessary.

EXPERIMENTAL

Initial aldehydes **IIa**–**IIh** and potassium carbonate were commercial products (Acros Organics) which were used without additional purification. Fluorinated β-oxo esters **Ia**–**Ie** were synthesized according to the procedure described in [32], and ionic liquids **A**–**C** were prepared as reported in [33–35]. The progress of reactions was monitored by thin-layer chromatography using Silufol plates (eluent benzene–ethyl acetate, 9:1; development with UV irradiation or by treatment with iodine vapor). The products were purified by column chromatography on silica gel (0.060–0.200 mm; Acros Organics). A 1.6-l Reltec 1/100 TH ultrasonic bath (operating frequency 47 kHz) was used for ultrasonic activation. The ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer at 300.13 MHz; the ^{13}C NMR spectra were measured on a Bruker Avance-300 instrument at 75 MHz; and the ^{19}F NMR spectra were obtained on a Bruker AC-200 spectrometer at 188.31 MHz. The IR spectra were measured in KBr on a Specord M-82 spectrometer. The elemental compositions were determined on a Perkin–Elmer 2400 analyzer.

4-Substituted 2,6-bis(fluoroalkyl)-2,6-dihydroxytetrahydro-2*H*-pyran-3,5-dicarboxylates IIIa–IIIm (*general procedure*). A mixture of 2.0 mmol of β-oxo ester **Ia**–**Ie**, 1.0 mmol of aldehyde **IIa**–**IIh**, 0.9 mmol of 1-butyl-3-methylimidazolium tetrafluoroborate, and 0.3 mmol of potassium carbonate was heated for 5–20 h at 65°C in an ultrasonic bath until the initial compounds disappeared (TLC). The mixture was cooled and extracted in succession with benzene (2×5 ml) and diethyl ether (2×5 ml). The extracts were combined, washed with water (3×25 ml), and dried over $MgSO_4$, the solvent was reduced under reduced pressure (40°C, 40 mm), and the residue was purified by column chromatography on silica gel using in succession hexane, hexane–benzene (1:1), and benzene as eluents.

Diethyl 2,6-dihydroxy-4-(4-nitrophenyl)-2,6-bis(trifluoromethyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIa). Reaction time 7 h. Yield 81%, mp 141–143°C. IR spectrum, ν, cm^{-1}: 3420 (OH), 1718 (C=O), 1190–1168 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t (6H, CH_3, J = 7.2 Hz), 3.27 d (2H, 3-H, 5-H, J = 12.04 Hz), 3.9 q (4H, OCH_2, J = 7.2 Hz), 4.13 t (1H, 4-H, J = 12.04 Hz), 5.63 s (2H, OH), 7.3 d (2H, *o*-H, J = 8.7 Hz), 8.25 d (2H, *m*-H, J = 8.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.5 (CH_3), 39.9 (C^4), 48.0 (C^3, C^5), 62.6 (OCH_2), 94.9 (C^2, C^6), 123.2 (CF_3), 124.01 (C^m), 129.7 (C^o), 142.5 (C^i), 148.1 (C^p), 166.9 (C=O). ^{19}F NMR spectrum ($CDCl_3$): δ_F − 85.17 ppm, s (CF_3). Found, %: C 44.15; H 3.75; F 21.80; N 2.64. $C_{19}H_{19}F_6NO_9$. Calculated, %: C 43.92; H 3.69; F 21.96; N 2.70.

Diethyl 2,6-dihydroxy-4-phenyl-2,6-bis(trifluoromethyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate

(IIIb). Reaction time 8 h. Yield 74%, mp 118–119°C; published data [28, 29]: yield 43% in the system EtOH–KF at 78°C, mp 116–118.5°C.

Diethyl 2,6-dihydroxy-4-(4-methoxycarbonylphenyl)-2,6-bis(trifluoromethyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIc). Reaction time 12 h. Yield 88%, mp 165–167°C. IR spectrum, ν, cm^{-1}: 3472 (OH), 1720 (C=O), 1212–1188 (C–F). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.75 t (6H, CH_3, J = 6.62 Hz), 3.46 d (2H, 3-H, 5-H, J = 12.02 Hz), 3.5–3.7 m (4H, OCH_2), 3.87 s (3H, OCH_3), 4.2 t (1H, 4-H, J = 12.02 Hz), 7.57 br.s (2H, *o*-H), 7.87 d (2H, *m*-H, J = 8.1 Hz), 8.11 br.s (2H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.4 (CH_3), 37.9 (C^4), 49.1 (OCH_3), 52.1 (C^3, C^5), 60.2 (OCH_2), 94.4 (C^2, C^6), 119.9 (CF_3), 123.7 (C^m), 128.9 (C^i), 129.7 (C^o), 142.6 (C^p), 166.9 (C=O). ^{19}F NMR spectrum (DMSO-d_6): δ_F −81.95 ppm, s (CF_3). Found, %: C 47.49; H 4.21; F 21.30. $C_{21}H_{22}F_6O_9$. Calculated, %: C 47.38; H 4.17; F 21.41.

Diethyl 4-(4-chlorophenyl)-2,6-dihydroxy-2,6-bis(trifluoromethyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIId). Reaction time 7 h. Yield 79%, mp 124–125.5°C. IR spectrum, ν, cm^{-1}: 3340 (OH), 1712 (C=O), 1112–1084 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t (6H, CH_3, J = 7.12 Hz), 3.19 d (2H, 3-H, 5-H, J = 12.3 Hz), 3.88 q (4H, OCH_2, J = 7.12 Hz), 3.90 t (1H, 4-H, J = 12.3 Hz), 5.71 br.s (2H, OH), 7.25 d (2H, *o*-H, J = 8.36 Hz), 7.35 d (2H, *m*-H, J = 8.36 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.4 (CH_3), 39.6 (C^4), 48.5 (C^3, C^5), 62.5 (OCH_2), 94.9 (C^2, C^6), 121.4 (CF_3), 129.2 (C^m), 129.8 (C^o), 133.4 (C^i), 134.8 (C^p, 170.4 (C=O). ^{19}F NMR spectrum ($CDCl_3$): δ_F −85.32 ppm, s (CF_3). Found, %: C 45.01; H 3.82; Cl 7.05; F 22.28. $C_{19}H_{19}ClF_6O_7$. Calculated, %: C 44.85; H 3.76; Cl 6.97; F 22.40.

Diethyl 2,6-dihydroxy-4-(4-methoxyphenyl)-2,6-bis(trifluoromethyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIe). Reaction time 20 h. Yield 70%, mp 97–98°C; published data [28]: yield 38% in the system EtOH–KF at 78°C, mp 95–96°C.

Diethyl 2,6-dihydroxy-4-(3-thienyl)-2,6-bis(trifluoromethyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIf). Reaction time 6 h. Yield 78%, mp 108–109°C. IR spectrum, ν, cm^{-1}: 3370 (OH), 1710 (C=O), 1220–1020 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (6H, CH_3, J = 7.09 Hz), 3.17 d (2H, 3-H, 5-H, J = 12.22 Hz), 3.96 q (4H, OCH_2, J = 7.09 Hz), 4.02 t (1H, 4-H, J = 12.22 Hz), 5.77 br.s (2H, OH), 7.02 d (1H, 5′-H, ^3J = 4.82 Hz), 7.16 d (1H, 2′-H, J = 2.84 Hz), 7.32 d.d (1H, 4′-H, J = 2.84, 4.82 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.4 (CH_3), 35.5 (C^4), 48.3 (C^3, C^5), 62.4 (OCH_2), 94.0 (C^2, C^6), 121.4 (CF_3); 124.5, 126.1, 126.8, 135.5 (C_4H_3S); 170.8 (C=O). ^{19}F NMR spectrum ($CDCl_3$): δ_F −85.42 ppm, s (CF_3). Found, %: C 42.65; H 3.89; F 23.61; S 6.53. $C_{17}H_{18}F_6SO_7$. Calculated, %: C 42.51; H 3.78; F 23.73; S 6.67.

Diethyl 2,6-dihydroxy-4-(pyridin-3-yl)-2,6-bis(trifluoromethyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIg). Reaction time 5 h. Yield 85%, mp 126–128°C; published data [31]: yield 20% in the system EtOH–piperidine at 20°C, mp 126–127°C.

Diethyl 4-ethyl-2,6-dihydroxy-2,6-bis(trifluoromethyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIh). Reaction time 6 h. Yield 80%, mp 123–125°C; published data [28]: yield 62% in the system EtOH–KF at 78°C; mp 125–127.5°C.

Dimethyl 2,6-bis(heptafluoropropyl)-2,6-dihydroxy-4-(4-nitrophenyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIi). Reaction time 7 h. Yield 80%, mp 148–150°C. IR spectrum, ν, cm^{-1}: 3400 (OH), 1724 (C=O), 1236–1128 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.42 m (8H, OCH_3, 3-H, 5-H), 4.12 t (1H, 4-H, J = 12.0 Hz), 5.92 s (2H, OH), 7.48 d (2H, *o*-H, J = 8.1 Hz), 8.25 d (2H, *m*-H, J = 8.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 40.1 (C^4), 47.1 (C^3, C^5), 53.3 (OCH_3), 98.0 (C^2, C^6), 109–122.9 m ($CF_2CF_2CF_3$), 124.5 (C^m), 129.5 (C^o), 142.1 (C^i), 148.3 (C^p), 170.3 (C=O). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: −80.91 s (6F, CF_3), −119.82 and −122.55 (4F, CF_2, *AB* system, J_{AB} = 278.0 Hz), −123.72 s (4F, C**F**$_2$CF$_3$). Found, %: C 36.63; H 2.28; F 38.33; N 2.11. $C_{21}H_{15}F_{14}NO_9$. Calculated, %: C 36.48; H 2.19; F 38.47; N 2.03.

Dimethyl 4-(4-chlorophenyl)-2,6-bis(heptafluoropropyl)-2,6-dihydroxytetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIj). Reaction time 12 h. Yield 71%, mp 127–129°C. IR spectrum, ν, cm^{-1}: 3360 (OH), 1715 (C=O), 1250–1118 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.30 d (2H, 3-H, 5-H, J = 12.2 Hz), 3.41 s (6H, OCH_3), 3.90 t (1H, 4-H, J = 12.2 Hz), 5.97 s (2H, OH), 7.18 d (2H, *o*-H, J = 7.4 Hz), 7.33 d (2H, *m*-H, J = 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 39.8 (C^4), 47.4 (C^3, C^5), 53.1 (OCH_3), 97.9 (C^2, C^6), 102.2–122.5 m ($CF_2CF_2CF_3$), 129.2 (C^m), 129.3 (C^o), 133.0 (C^i), 134.9 (C^p), 171.3 (C=O). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: −80.94 t (6F, CF_3, J = 10.0 Hz), −120.22 and −122.38 (4F, CF_2, *AB* system, J_{AB} = 283.0 Hz), −123.74 m (4F, C**F**$_2$CF$_3$).

Found, %: C 37.12; H 2.29; Cl 5.37; F 39.19. $C_{21}H_{15}ClF_{14}O_7$. Calculated, %: C 37.05; H 2.22; Cl 5.31; F 39.07.

Diethyl 2,6-dihydroxy-4-(4-nitrophenyl)-2,6-bis-(1,1,2,2-tetrafluoroethyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIk). Reaction time 18 h. Yield 75%, mp 137–139°C. IR spectrum, ν, cm^{-1}: 3364 (OH), 1704 (C=O), 1220–1016 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (6H, CH_3, J = 7.2 Hz), 3.36 d (2H, 3-H, 5-H, J = 12.3 Hz), 3.88 q (4H, OCH_2, J = 7.2 Hz), 4.02 t (1H, 4-H, J = 12.3 Hz), 5.98 s (2H, OH), 6.15 t.t (2H, CHF_2, J = 6.3, 52.6 Hz), 7.50 d (2H, *o*-H, J = 8.8 Hz), 8.23 d (2H, *m*-H, J = 8.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.3 (CH_3), 40.0 (C^4), 45.5 (C^3, C^5), 62.5 (OCH_2), 96.4 (C^2, C^6), 108.0 (CF_2), 113.0 (CHF_2), 123.9 (C^m), 129.7 (C^o), 142.2 (C^i), 148.0 (C^p), 170.8 (C=O). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: −130.7 d (4F, CF_2, J = 274.6 Hz), −135.2 and −137.6 (4F, CHF_2, *AB* system, J_{AB} = 304.8, J_{FH} = 52.6 Hz). Found, %: C 43.37; H 3.70; F 26.11; N 2.34. $C_{21}H_{21}F_8NO_9$. Calculated, %: C 43.24; H 3.63; F 26.05; N 2.40.

Dimethyl 2,6-dihydroxy-4-(4-nitrophenyl)-2,6-bis(1,1,2,2,3,3,4,4-octafluorobutyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIl). Reaction time 12 h. Yield 86%, mp 129–130.5°C. IR spectrum, ν, cm^{-1}: 3440 (OH), 1716 (C=O), 1220–1092 (C–F). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.24 s (6H, OCH_3), 3.60 d (2H, 3-H, 5-H, J = 11.92 Hz), 4.33 t (1H, 4-H, J = 11.92 Hz), 7.0 t (2H, CHF_2, J = 50.3 Hz), 7.72 br.s (2H, *o*-H), 7.93 s (2H, OH), 8.20 d (2H, *m*-H, J = 7.97 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 40.5 (C^4), 47.5 (C^3, C^5), 53.3 (OCH_3), 98.2 (C^2, C^6), 124.1 (C^m), 124.17–122.28 m ($CF_2CF_2CF_2$), 128.9 (C^o), 129.5 (CHF_2), 142.1 (C^i), 148.3 (C^p), 170.8 (C=O). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: −117.3 and −120.0 (4F, α-CF_2, *AB* system, J_{AB} = 282.8 Hz), −120.06 m (4F, β-CF_2), −128.96 m (4F, γ-CF_2), −137.30 d (4F, CHF_2, J = 50.1 Hz). Found, %: C 36.73; H 2.35; F 40.11; N 1.93. $C_{23}H_{17}F_{16}NO_9$. Calculated, %: C 36.57; H 2.27; F 40.24; N 1.85.

Dimethyl 2,6-dihydroxy-4-(4-nitrophenyl)-2,6-bis(nonafluorobutyl)tetrahydro-2*H*-pyran-3,5-dicarboxylate (IIIm). Reaction time 9 h. Yield 85%, mp 118–120°C. IR spectrum, ν, cm^{-1}: 3420 (OH), 1728 (C=O), 1236–1104 (C–F). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.25 s (6H, OCH_3), 3.69 d (2H, 3-H, 5-H, J = 11.77 Hz), 4.36 t (1H, 4-H, J = 11.77 Hz), 7.75 br.s (2H, *o*-H), 8.07 s (2H, OH), 8.20 d (2H, *m*-H, J = 8.6 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 40.3 (C^4), 47.5 (C^3, C^5), 53.4 (OCH_3), 98.3 (C^2, C^6), 124–129 m ($CF_2CF_2CF_2CF_3$), 124.1 (C^m), 128.9 (C^o), 142.1 (C^i), 148.3 (C^p), 170.8 (C=O). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: −79.55 t (6F, CF_3, J = 9.9 Hz), −117.3 and −119.8 (4F, α-CF_2, *AB* system, J_{AB} = 282.6 Hz), −119.2 m (4F, β-CF_2), −125.24 m (4F, γ-CF_2). Found, %: C 35.07; H 1.99; F 43.05; N 1.89. $C_{23}H_{15}F_{18}NO_9$. Calculated, %: C 34.91; H 1.91; F 43.21; N 1.77.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 06-03-32603).

REFERENCES

1. Yanovskaya, L.A., Kryshtal', G.V., and Kul'ganek, V.V., *Usp. Khim*., 1984, vol. 53, p. 1280.
2. Tietze, L.F., *Comprehensive Organic Synthesis: Selectivity, Strategy, and Efficiency in Modern Organic Chemistry*, Trost, B.M. and Fleming, I., Eds., Oxford: Pergamon, 1991, vol. 2, p. 341.
3. Gardner, P.D. and Brandon, R.L., *J. Org. Chem*., 1957, vol. 22, p. 1704.
4. Gnanadickam, C., *Ann. Chim*., 1962, vol. 7, p. 826.
5. Jones, G., *Organic Reactions*, Cope, A.C., Ed., New York: Wiley, 1967, vol. 15, p. 204.
6. Nitta, H., Takimoto, K., and Veda, L., *Chem. Pharm. Bull*., 1992, vol. 40, p. 858.
7. Niwas, S., Kumar, S., and Bhaduri, A.P., *Indian J. Chem., Sect. B*, 1985, vol. 24, p. 747.
8. Aftanasi, O., Filippone, P., and Mai, A., *Synth. Commun*., 1983, vol. 13, p. 1203.
9. Danion-Bougot, R. and Carrie, R., *Bull. Soc. Chim. Fr*., 1968, p. 2526.
10. Loeller, J.R., *Tetrahedron Lett*., 1989, vol. 30, p. 1457.
11. Mayer, H., Bossert, F., Wehinger, E., Stoeple, K., and Vater, W., *Arzneim.-Forsch*., 1981, vol. 31, p. 407.
12. Gein, V.L., Gein, N.V., Voronina, E.V., and Kriven'-ko, A.P., *Khim.-Farm. Zh*., 2002, vol. 36, p. 23.
13. Bao, W., Wang, L., and Li, Y., *J. Chem. Res., Synop*., 2003, p. 294.
14. Su, C., Chen, L.-C., and Zheng, Q.-G., *Synthesis*, 2003, no. 4, p. 555.
15. Morrison, D.W., Forbes, D.C., and Davis, J.H., *Tetrahedron Lett*., 2001, vol. 42, p. 6053.
16. Formentin, P., Garcia, H., and Leyva, A., *J. Mol. Catal. A: Chem*., 2004, vol. 214, p. 137.
17. Hangarge, R.V. and Shingare, M.S., *Mendeleev Commun*., 2003, no. 2, p. 79.
18. Hangarge, R.V., Jarikote, D.V., and Shingare, M.S., *Green Chem*., 2002, vol. 4, p. 266.

19. Khan, F.A., Dash, J., Satapathy, R., and Upadhyay, S.R., *Tetrahedron Lett*., 2004, vol. 45, p. 3055.
20. Shestopalov, A.M., Zlotin, S.G., Shestopalov, A.A., Mortikov, V.Yu., and Rodinovskaya, L.A., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2004, p. 546.
21. Welton, T., *Chem. Rev*., 1999, vol. 99, p. 2071.
22. Zhao, D., Wu, M., Kou, Y., and Min, E., *Catal. Today*, 2002, vol. 74, p. 157.
23. Olivier-Bourbigou, H. and Magna, L., *J. Mol. Catal. A: Chem*., 2002, vols. 182–183, p. 419.
24. *Ionic Liquids in Synthesis*, Wasserscheid, P. and Welton, T., Eds., Weinheim: Wiley, 2003, p. 363.
25. Davis, J.H. and Fox, P.A., *Chem. Commun*., 2003, p. 1209.
26. Zlotin, S.G., Bogolyubov, A.V., Kryshtal, G.V., Zhdankina, G.M., Struchkova, M.I., and Tartakovsky, V.A., *Synthesis*, 2006, p. 3849.
27. Zlotin, S.G., Kryshtal', G.V., Zhdankina, G.M., Bogolyubov, A.V., Postikova, S.G., and Tartakovskii, V.A., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2007, p. 1431.
28. Dey, A.S. and Joullie, M.M., *J. Org. Chem*., 1965, vol. 30, p. 3237.
29. Pryadeina, M.V., Kuzueva, O.G., Burgart, Ya.V., and Saloutin, V.I., *Russ. J. Org. Chem*., 2002, vol. 38, p. 224.
30. Pryadeina, M.V., Kuzueva, O.G., Burgart, Ya.V., Saloutin, V.I., Lyssenko, K.A., and Antipin, M.Yu., *J. Fluorine Chem*., 2002, vol. 117, p. 1.
31. Balicki, R. and Nantka-Namirski, P., *Pol. J. Chem*., 1981, vol. 55, p. 2439.
32. Lovelace, A.M., Rausch, D.A., and Postelnek, W., *Aliphatic Fluorine Compounds*, New York: Reinhold, 1958. Translated under the title *Alifaticheskie ftorsoderzhashchie soedineniya*, Moscow: Inostrannaya Literatura, 1961, p. 225.
33. Suarez, P.A., Dullius, J.E.L., Einloft, S., De Souza, R.F., and Dupont, J., *Polyhedron*, 1996, vol. 15, p. 1217.
34. Bonhôte, P., Dias, A.-P., Papageorgiou, N., Kalyanasundaram, K., and Grätzel, M., *Inorg. Chem*., 1996, vol. 35, p. 1168.
35. MacFarlane, D.R., Meakin, P., Sun, J., Amini, N., and Forsyth, M., *J. Phys. Chem. B*, 1999, vol. 103, p. 4164.