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Isomerism and Tautomerism of 5-Fluoroalkyl-Substituted 3-Acetyldihydrofuran-2(3*H*)-ones

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Abstract—The geometric isomerism and tautomeric equilibrium of 5-fluoroalkyl-3-acetyldihydrofuran-2(3*H*)-ones obtained by condensation of (perfluoroalkyl)methyloxiranes with acetoacetic ester were studied. In the solid state the acyl-γ-lactones are in diketo form, mainly as *cis* isomer, whose structure is confirmed by the data of X-ray structural investigation, while in solution an equilibrium exists of *cis-trans* isomers and an enol form, as established by 1D and 2D methods of ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

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The γ-lactone ring is an important structural fragment of many natural and biologically active compounds [1, 2]. On the basis of functionalized γ-lactones the components of new perfumes, sex attractants, plant growing regulators have been created. They were used to obtain macrocyclic antibiotics and natural feromones and alkaloids and for the preparation of pharmaceuticals for treatment leukemia and other diseases.

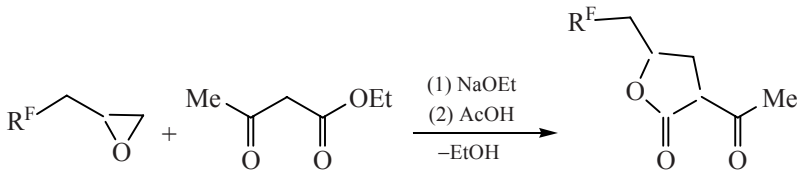
Despite a variety of the methods of synthesis of fluorine-containing γ-lactones already published [3–7] there is no universal procedure providing high yield of the target compounds. The so far developed synthetic methods are multistep and labor-consuming; the reagents are difficultly accessible, and the yields of the fluorine-containing γ-lactones are relatively low.

The introduction of an additional carboxylic group to C^3 position of the γ-lactone ring provides new derivatives belonging to the class of β-dicarbonyl compounds that are characterized by a keto-enol equilibrium. When the lactone contains other substituents, it can exist also as two geometric isomers. However, there is no published data concerning the geometric isomerism and tautomeric equilibria of such compounds.

This work concerns the synthesis, the study of isomeric composition and the keto-enol tautomerism in the series of 5-polyfluoroalkyl-3-acetyldihydrofuran-2 (3*H*)-ones.

The simplest and the most convenient scheme of the synthesis of 5-perfluoroalkyl- substituted γ-lactones is the condensation of a fluorine-containing oxirane with acetoacetic ester in the presence of a base [8]. We prepared the fluorine-containing γ-lactones, 3-acetyl-5-fluoroalkyl-dihydrofuran-2(3H)-ones (**IIa–IIc**) by this method (Scheme 1) starting with

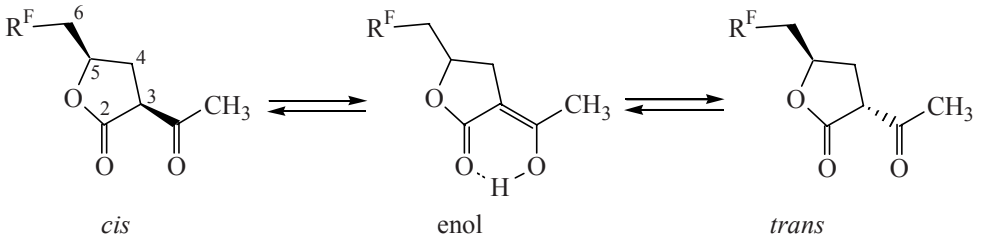
Scheme 1.



Ia–Ic **IIa–IIc**

R^F = C_2F_5 (**a**), C_3F_7 (**b**), C_4F_9 (**c**).

Scheme 2.



(perfluoroalkyl)methyloxiranes (**Ia–Ic**) that we have described earlier [9].

α-Acetyl-γ-butyrolactones **IIa–IIc** like other 1,3-ketoesters represent a prototropic system and can exist in enol and diketone tautomeric forms, therewith, when there are other substituents in the γ-lactone ring, the diketone form can exist as two geometric isomers (Scheme 2).

Unlike the 2-acylcycloalkanones, α-acyllactones exist predominantly in the diketone form. For example, α-acetyl-γ-butyrolactone dissolved in methanol is enolized only to 22% [10]. The content of the enol form in 3-acetyl-5-alkylbutyrolactones in various solvents is from 10 to 23% [11], but the ratio of geometric isomers of diketone form is not reported. The *cis*- and *trans*-isomers of 5-fluoroalkyl-containing γ-lactones with 3-(ethoxycarbonyl)methyl substituent have been isolated and characterized in [3], but the assignment of the geometric isomers was based only on the value of the vicinal spin-spin coupling constant of the protons at C^4 and C^5 that we believe to be insufficient evidence of their assignment to *cis* or *trans* series. Tautomeric equilibrium and geometric isomerism of 3-acetyl-5-perfluorohexyldihydrofuran-2(3*H*)-one has not been considered [8].

In the IR spectra of compounds **IIa–IIc** in solid state there are strong bands near 1770 and 1720 cm^{-1} related to the keto form (see Experimental), but the spectra of their solutions in chloroform besides the bands of diketone form contain a weak band at 1653 cm^{-1} which can be assigned to the enol form.

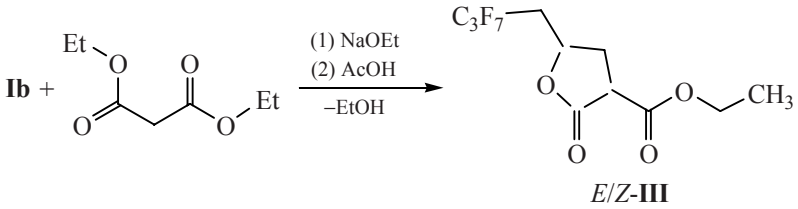
In the present work the study of tautomeric equilibrium and geometric isomerism of the synthesized compounds **IIa–IIc** was carried out using various methods of ^1H, ^{13}C and ^{19}F NMR spectroscopy including ^1H–^{19}F double frequency and two-dimensional homo- and heteronuclear experiments.

The fairly complicated appearance of ^1H NMR spectra of γ-lactones **IIa–IIc** provides difficulties in the elucidation of quantitative and qualitative composition of the studied compounds. In $CDCl_3$ the compounds **IIa–IIc** exist as a mixture of three forms (Scheme 2), and even at operating frequency 400 MHz the proton signals related to either the same or to different forms are partially overlapping. The signals of OH protons at 10.86 ppm and the triplet of methyl group at 2.00 ppm with long-range spin-spin coupling constant ^5J = 1.2 Hz related to enol form can be identified rather easily. Also, the singlets of CH_3 groups of diketone form stereoisomers (δ 2.44 and 2.49 ppm) can be clearly distinguished, but they fall to the same chemical shift range (2.20–2.60 ppm) where occur the signals of nonequivalent protons of methylene groups at C^4 and C^6 in all the three forms. The separately located multiplets at δ 3.00 and 3.14 ppm, as can be judged from their low intensity, belong to some minor forms. In the region of 4.80–5.00 ppm occur overlapping multiplets of the protons at C^5 in all three forms. The protons at C^3 exist only in diketone forms, their signals have simple multiplicity (doublet of doublets), but the signals of *cis*- and *trans*-isomer are also overlapping. Thus, the analysis of tautomeric and isomeric compositions of γ-lactones **IIa–IIc** requires reliable identification of signals in the ^1H NMR spectra characteristic of each form.

As a model compound for studying geometric isomers of substituted γ–lactones we took γ-lactone **III** synthesized according to Scheme 3.

Compound **III** exists only in the diketone form, and its ^1H NMR spectrum resembles in general those of acetyl-γ-lactones **IIa–IIc** but there are certain differences: (1) no signals of enol form; (2) the region of the signals of methylene protons is not overlapped by the signals of methyl groups; (3) the signals of the protons at C^5 are not overlapped but in this case they appear as separate multiplets at δ 4.87 and 5.06 ppm, with the integral intensities ratio 60 **:** 40. The latter situation makes it possible, on the one hand, to determine relative content of geometric isomers by

Scheme 3.



E/*Z*-**III**

integration of the respective signals and, on the other hand, to apply the selective methods of NMR spectroscopy. Actually, in the 1D TOCSY spectra with selective excitation of the resonance of the protons at C^5 in different isomers of lactone **III** the signals of respective spin systems become selectable. The ^1H–$\{^{19}F\}$ NMR spectrum obtained with decoupling of the protons from the fluorine nuclei in α-CF_2 group further simplifies the spectral picture, in particular in the region of the signals of methylene protons (Fig. 1). Analysis of results of these experiments allows elucidate all NMR parameters (δ_H and J_{HH}) of all non-equivalent protons in two geometric isomers of compound **III** (Table 1).

The relative configuration of geometric isomers of compound **III** is revealed by the application of nuclear Overhauser effect in 2D ^1H –^1H NOESY experiment. Comparing the volume integral intensities of the cross peaks between the protons H^3, H^{4a}, H^{4b}, and H^5 in the isomeric structures allows a conclusion that the dominat isomer has *cis* configuration while the minor one is *trans*. Actually, for the major structure cross peaks occur between the signals of protons H^3 and H^5 on one hand and low field signal of the proton H^{4a}, while the cross peaks (H^3, H^{4b}) and (H^5, H^{4b}) are of relatively low intensity. For the minor *trans*-isomer, on the contrary, the cross peaks (H^3, H^{4b}) and (H^5, H^{4a}) are more intense than (H^3, H^{4a}) and (H^5, H^{4b}). But even more spectacular in this respect is intensity of cross peaks between the signals of H^3 and H^5 protons: for the *cis*-isomer the intensity of this peak is by an order of magnitude greater than that for the *trans* isomer (Fig. 2).

Table 1. Parameters of ^1H NMR spectrum of compound **III** (cyclic protons)

Isomer	Chemical shifts, δ, ppm and spin–spin coupling constants, *J*, Hz			
	H^3	H^{4a}	H^{4b}	H^5
cis	3.70 d.d $J_{3,4b}$ 10.5 $J_{3,4a}$ 9.2	2.77 d.d.d $J_{4a,4b}$ 13.2 $J_{4a,3}$ 9.2 $J_{4a,5}$ 6.4	2.48 d.d.d $J_{4b,4a}$ 13.2 $J_{4b,3}$ 10.5 $J_{4b,5}$ 9.1	4.87 d.d.d.d $J_{5,4b}$ 9.1 $J_{5,6a}$ 6.5 $J_{5,4a}$ 6.4 $J_{5,6b}$ 6.0
trans	3.64 d.d $J_{3,4b}$ 9.4 $J_{3,4a}$ 3.5	2.87 d.d.d $J_{4a,4b}$ 13.3 $J_{4a,5}$ 6.5 $J_{4a,3}$ 3.5	2.28 d.d.d $J_{4b,4a}$ 13.3 $J_{4b,3}$ 9.4 $J_{4b,5}$ 8.3	5.06 d.d.d.d $J_{5,4b}$ 8.3 $J_{5,6a}$ 6.7 $J_{5,4a}$ 6.5 $J_{5,6b}$ 5.9

The typical difference in the appearance of ^1H NMR spectra of two geometric isomers of compound **III** is seen from the data in Table 1 . The proton H^3 of the major *cis*-isomer is strongly and almost equally coupled with H-4 protons, $J_{3,4a} \approx J_{3,4b}$, while in the minor isomer the respective constants noticeably differ by value. Besides, the notable difference in the nonequivalence in the chemical shifts of diastereotopic protons at C^4 calls for attention: in the *trans* isomer [$\Delta_{ab} = \delta(H^{4a})–\delta(H^{4b}) = 0.59$ ppm] it is certainly larger than in the *cis* isomer($\Delta_{ab} = 0.29$ ppm).

The same is true for the case of ^1H NMR spectra of the diketone form isomers of 3-acetyl-γ-lactones **IIa–IIc**. In all cases the signal of H^3 proton of the dominat *cis* isomer is shaped as a triplet ($J_{3,4a} = J_{3,4b} = 9.3$ Hz), while that of *trans* isomer as a doublet of doublets ($J_{3,4b}$ = 9.1–9.3, $J_{3,4a}$ = 3.1–3.3 Hz). For the *trans* isomer of diketone form of compounds **IIa–IIc** a big nonequivalence of diastereotopic protons at the C^4 atom ($\Delta_{ab} \approx 1$ ppm) as compared with the *cis* isomers also is typical, as clearly seen in ^1H–$\{^{19}F\}$ spectra at the decoupling from the fluorine nuclei in α-CF_2 group.

Thus, we completely assigned the signals in the ^1H NMR spectra of lactones **IIa–IIc** and elucidated the signals appropriate for qualitative determination of the contributions of different forms and isomers. For the enol form these signals are those of CH_3 and OH groups and a signal of H^{4a} at δ 3.15 ppm (ddq, ^2J = 14.9, ^3J = 8.5, ^5J = 1.2 Hz), for the *trans* isomer the

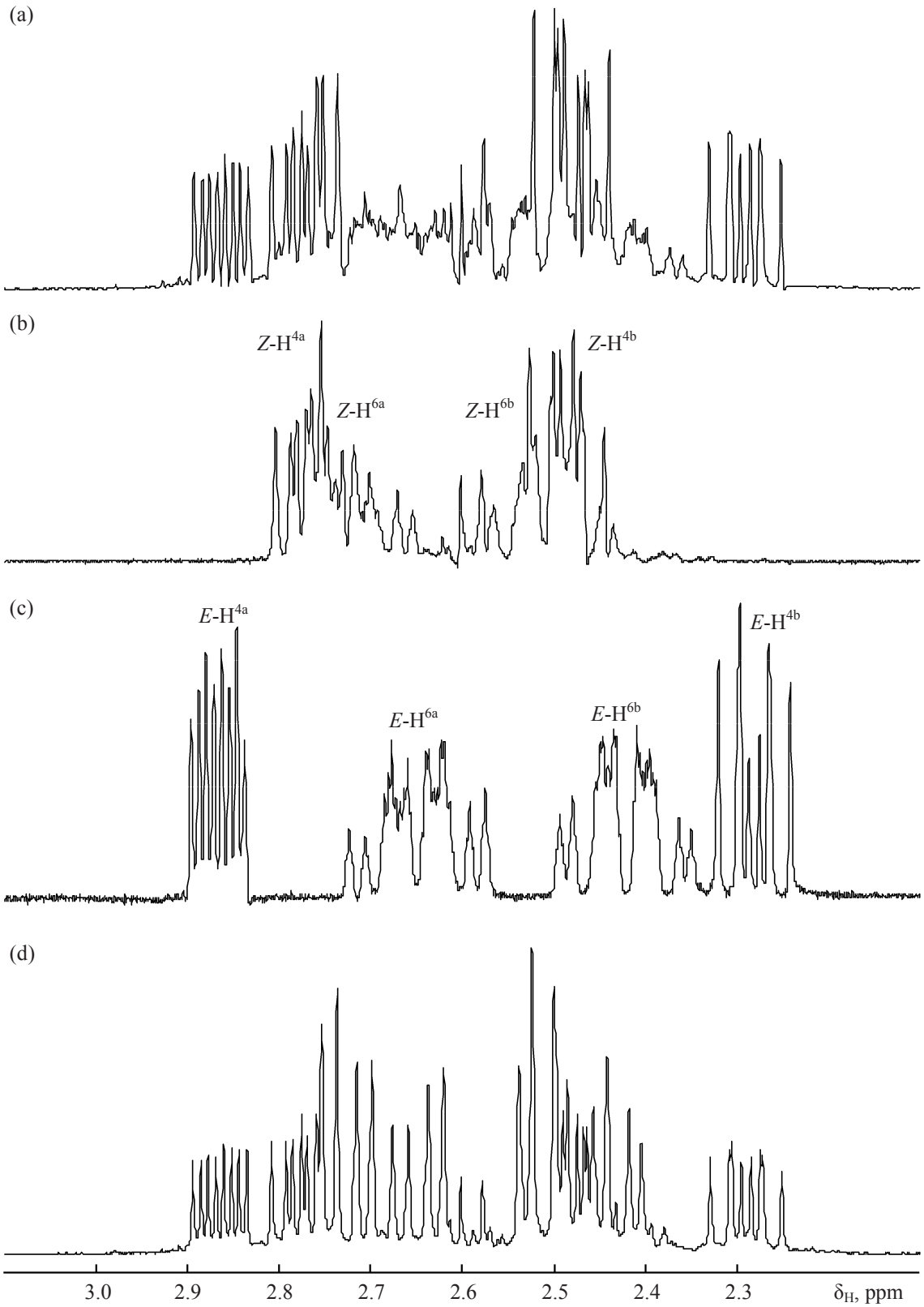


Fig. 1. ^{1}H NMR spectra of compound **III** in the region of methylene protons: (a) ^{1}H NMR spectrum (400 MHz, $CDCl_3$); (b) 1D TOCSY spectrum at selective excitation of *cis*-H^5 proton, δ_H 4.87 ppm; (c) 1D TOCSY spectrum at selective excitation of *trans*-H^5 proton, δ_H 5.06 ppm; and (d) ^{1}H–{^{19}F} double resonance spectrum.

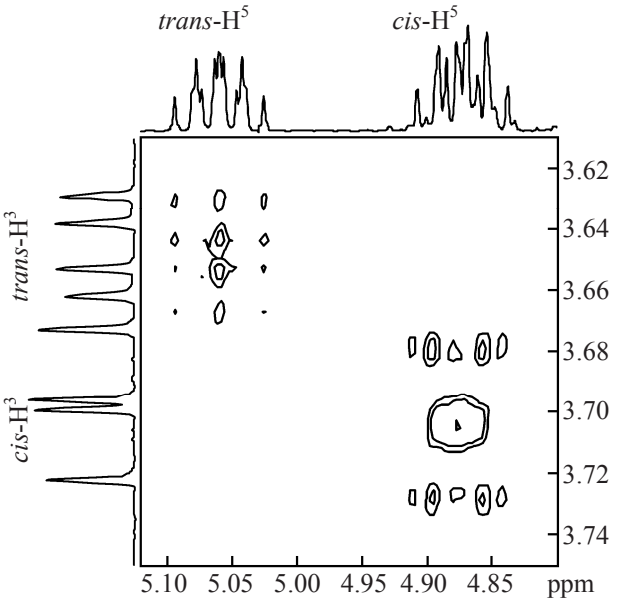


Fig. 2. A fragment of 2D ^{1}H –^{1}H NOESY spectrum of compound **III**.

signals of non-equivalent protons at C^4: δ 3.00 ppm (d.d.d, H^{4a}, J = 13.3, 6.8, 3.2 Hz) and δ 2.06 ppm (d.d.d, H^{4b}, J = 13.3, 9.0, 8.9 Hz).

In the ^{13}C NMR spectra of compounds **IIa–IIc** appear three sets of signals corresponding to three forms of the γ-lactones. Combining two-dimensional heteronuclear experiments ^{1}H–^{13}C HSQC and HMBC we identified the signals of practically each carbon atom except those in perfluorinated substituents R^F (Table 2). In the spectrum of diketone form the signal of the carbon atom of acetyl carbonyl group appears at lower field [δ(CO) ≈ 199 ppm] compared to that of cyclic ester carbonyl [δ(C^2) ≈ 171 ppm]. In the spectrum of enol form the signal of cyclic carbonyl is shifted downfield by 3.5 ppm due to the formation of intramolecular hydrogen bond while the signal of acetyl carbonyl is shifted upfield by 30 ppm. The enolization of γ-lactones **IIa–IIc** results in an upfield shift by approximately 10 ppm of the signal of methyl carbon atom as compared with the diketone form.

The identification of the signals in ^{1}H NMR spectra made it possible to elucidate the ratio of different forms of lactones **IIa–IIc** in solution and to studying its variation in time. In the first moment after dissolution of compound **IIa–IIc** in $CDCl_3$ (3–5 min) *cis*-isomer of diketone form dominates in the solution: its relative content is 96–97%. In time, enol form and *trans* isomer of the diketone form appear in the solution, and during first 30–40 min the enol fraction becomes higher than that of the *trans* form. Then the relative content of enol remains constant while the fraction of the *trans* form grows. The equilibrium is achieved fairlyslowly, approximately after 200–220 h, therewith the enol form fraction is approximately the same in all the studied lactones **IIa–IIc**, about 14–15%, while the fraction of the formed *trans* isomer of the diketone form depends on the R^F substituent (Table 3). It is interesting to note that after evaporation of the solvent followed by again dissolving the product in $CDCl_3$, in the first moment again occurs initial ratio of the different form, and the *cis* isomer predominates. We believe this result to show that in the solid state the formation of the *cis* isomer is obviously advantageous

Table 2. The ^{13}C NMR data of lactones **IIa**, **IIb**

Compound	**IIa** ($R^F = C_2F_5$)			**IIb** ($R^F = C_3F_7$)		
isomer	*cis*	*trans*	enol	*cis*	*trans*	enol
atom	δ_C, ppm ($^nJ_{CF}$, Hz)					
CO	199.60	198.96	168.97	199.63	198.98	168.99
C^2	170.90	170.83	174.46	170.92	170.85	174.47
C^3	53.15	54.06	93.94	53.15	54.07	93.94
C^4	29.50	30.31	30.93	29.56	30.37	31.00
C^5	71.53 t (^3J 3.0)	72.88 t (^3J 2.5)	71.40 t (^3J 3.0)	71.52 t (^3J 3.2)	71.88 t (^3J 3.2)	71.40 t (^3J 2.9)
C^6	36.53 t (^2J 21.1)	36.51 t (^2J 21.2)	36.99 t (^2J 20.9)	36.48 t (^2J 20.7)	36.48 t (^2J 20.7)	36.96 t (^2J 20.7)
Me	29.63	28.93	19.21	29.64	28.93	19.21

thermodynamically, while in solution both the geometric isomer are approximately equally probable.

The tautomerism and accompanying isomerism of the lactones **IIa–IIc** are accelerated noticeably in the medium of acetic acid. When the solution in $CDCl_3$ contains equimolar amounts of compound **IIa** and acetic acid, even in the first moment 14% of enol form and 34% of *trans* isomer can be registered. At equilibrium that in this case is achieved approximately in 1 h the fractions of the diketone form *cis* and *trans* isomers are 45% and 40% respectively. When deuterated acid CD_3COOD is used, a deuteration occurs that probably proceeds via proton–deuterium exchange in the enol form and later becomes seen in the NMR spectra of the diketone form isomers. In the ^1H NMR spectrum integral intensity of the H^3 proton signal of diketone form falls and a change in multiplicity occurs of the nonequivalent protons at C^4. The degree of deuterium for proton replacement is 40% at the mole ratio 1 : 1 and achieves 80% with CD_3COOD excess. In the ^{13}C NMR spectra appears a second set of signals that corresponds to deuterated isomers of diketone form. The chemical shifts of signals differ from the initial ones due to isotopic effect, and signals of C^3 carbons appear as typical triplets with the constant $^1J_{CD}$ = 20 Hz.

The *cis* configuration of the synthesized acetyl-γ-lactones in crystal was confirmed by the data of X-ray structural analysis on the example of compound **IIb** (Fig. 3). The crystal packing (Fig. 4) is formed by two crystallographically independent molecules with similar bond lengths and bond angles parameters that on the whole are close to standard ones. The molecules are packed as the zigzags orthogonal to *b* axis of the elementary cell, the lactone rings form layers with centrosymmetrical dimers separated by polyfluoroalkyl groups. The oxygen atoms in this structure have short intermolecular contacts with the hydrogen atoms of the ring CH groups, the contacts lengths are by 0.11–0.21 Å less than the sum of van der Waals radii. This is understandable due to the enhanced CH-acid character of the lactone protons owing to *–I* effect of the ring oxygen atoms.

Thus, 5-fluoroalkyl-3-acetyl-dihydrofuran-2(3*H*)-ones that were synthesized by the condensation of fluorine-containing oxiranes and acetoacetic ester exist in the solid state predominantly as the diketone form *cis* isomer while in solution in $CDCl_3$ as an equilibrium mixture of the diketone *cis* and *trans* isomers and enol.

Table 3. Content (%) of enol and isomeric forms of lactones **IIa–IIc** in $CDCl_3$ at equilibrium

Compound no.	R^F	*cis*	*trans*	enol
IIa	C_2F_5	57	29	14
IIb	C_3F_7	49	37	14
IIc	C_4F_9	46	39	15

EXPERIMENTAL

The IR spectra were registered on a Perkin–Elmer Spectrum One B spectrophotometer from mulls in mineral oil. The ^1H, ^{13}C, and ^{19}F NMR spectra were registered on a Bruker DRX-400 instrument from solutions in $CDCl_3$, at operating frequencies 400.1, 100, and 376.5 MHz, respectively, with internal references Me_4Si and C_6F_6. Elemental analysis was carried out on an automatic Perkin–Elmer PE 2400 analyzer. The melting points were measured on a Stuart MP3 device.

A procedure for the synthesis of lactones IIa–IIc. To 75 ml of anhydrous ethanol was added 1.84 g (0.08 mol) of metallic sodium, and the reaction mixture was stirred until a homogenous solution formed. Then 10.34 g (0.08 mol) of acetoacetic acid was added dropwise, the reaction mixture was warmed to 30–35°C and 0.08 mol of compound **Ia–Ic** was added in 30 min. The mixture was stirred for 6–7 h and then acetic acid was added to pH 6–7 and the product was extracted with diethyl ether (3×30 ml). After removing the ether, the residue was distilled in a vacuum of oil pump and then recrystallized from ethanol.

3-Acetyl-5-(2,2,3,3,3-pentafluoropropyl)tetrahydrofuran-2-one (IIa): yield 46 %, white crystals, mp 66–67°C. The IR spectrum, ν, cm^{-1}: 1769, 1724 (C=O).

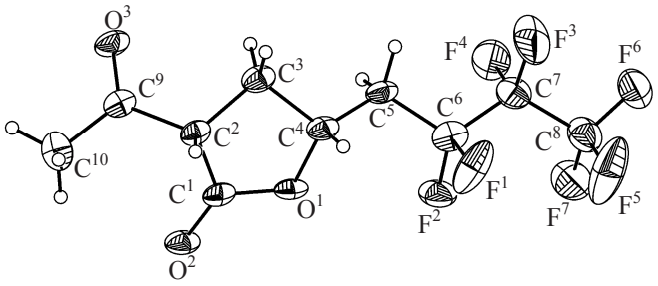


Fig. 3. General view of 3-acetyl-5-(2,2,3,3,4,4,4-heptafluorobutyl)tetrahydrofuran-2-one **IIb** molecule from the X-ray structural data, as thermal ellipsoids with 50% probability.

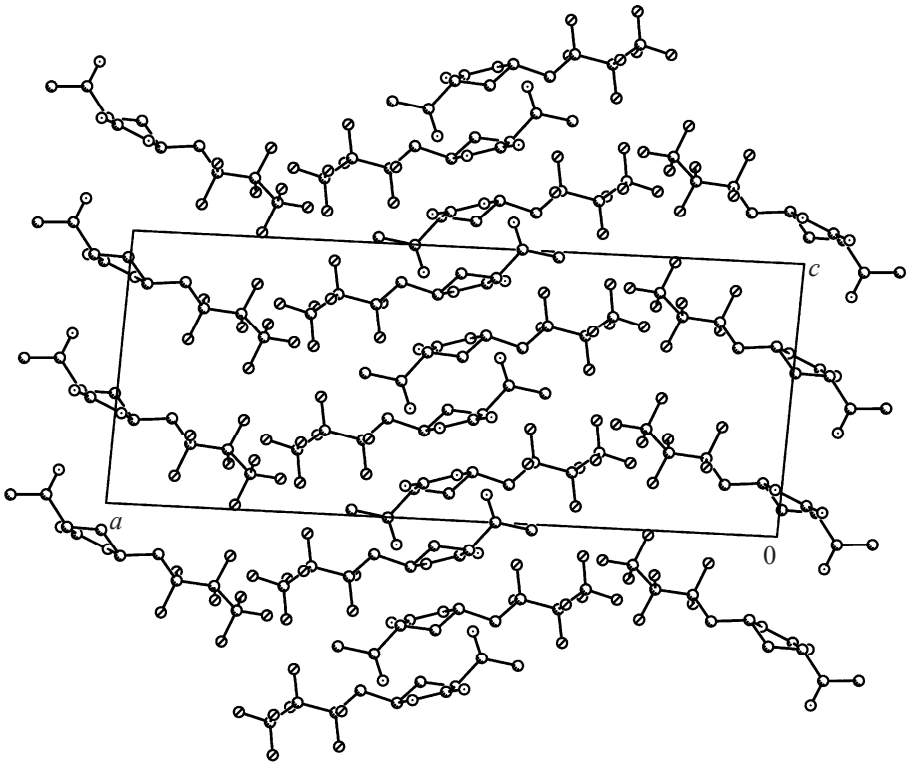


Fig. 4. Crystal package of compound **IIb**.

The ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 2.00 t (0.42H, enol-Me, *J* 1.2); 2.06 d.t (0.3H, *trans*-H^{4b}, *J* 13.3, 9.0); 2.27–2.71 m (5.84H, *cis, trans*-Me, H^6, *cis*-H^4, enol-H^{4b}); 3.00 d.d.d (0.3H, *trans*-H^{4a}, *J* 13.3, 6.8, 3.3); 3.14 d.d.q (0.14H, enol-H^{4a}, *J* 14.9, 8.5, 1.2); 3.78–3.86 m (0.86H, *cis, trans*-H^3); 4.80–4.96 m (1H, H^5), 10.86 s (0.14H, OH). The ^{19}F (δ, ppm, *J*, Hz): 45.04 m (1.12F, *cis*-CF_2); 45.10–45.26 m (0.88F, *trans,* enol-CF_2); 76.00 t (0.42F, enol-CF_3, *J* 1.0); 76.02 t (0.9F, *trans*-CF_3, *J* 1.0); 76.05 t (1.68F, *cis*-CF_3, *J* 1.0). Found, %: C 41.42; H 3.41; F 36.40. $C_9H_9F_5O_3$. Calculated, %: C 41.55; H 3.49; F 36.51.

3-Acetyl-5-(2,2,3,3,4,4,4-heptafluorobutyl)tetrahydrofuran-2-one (IIb): yield 53 %, white crystals, mp 66–67°C. The IR spectrum, ν, cm^{-1}: 1765, 1710 (C=O). The ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 2.00 t (0.42H, enol-Me, *J* 1.2); 2.06 d.t (0.37H, *trans*-H^{4b}, *J* 13.3, 9.0); 2.36–2.72 m (5.7H, *cis, trans*-Me, H^6, *cis*-H4, enol-H^{4b}); 3.02 d.d.d (0.37H, *trans*-H^{4a}, *J* 13.3, 6.7, 3.1); 3.15 d.d.q (0.14H, enol-H^{4a}, *J* 14.9, 8.5, 1.2); 3.78–3.86 m (0.86H, *cis, trans*-H^3); 4.81–4.98 m (1H, H^5), 10.86 s (0.14H, OH). The ^{19}F (δ, ppm): 33.9–34.03 m (2F, CF_2); 47.9–48.3 m (2F, CH_2CF_2); 81.34–81.44 m (3F, CF_3). Found, %: C 38.89; H 2.88; F 42.67. $C_{10}H_9F_7O_3$. Calculated, %: C 38.72; H 2.92; F 42.88.

3-Acetyl-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)tetrahydrofuran-2-one (IIc): yield 48%, white crystals, mp 69–70°C. The IR spectrum, ν, cm^{-1}: 1777, 1720 (C=O). The ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 2.00 t (0.45H, enol-Me, *J* 1.2); 2.07 d.t (0.4H, *trans*-H^{4b}, *J* 13.2, 9.0); 2.38–2.73 m (5.6H, *cis, trans*-Me, H^6, *cis*-H4, enol-H^{4b}); 3.01 d.d.d (0.4H, *trans*-H^{4a}, *J* 13.2, 6.8, 3.1); 3.15 d.d.q (0.15H, enol-H^{4a}, *J* 14.9, 8.5, 1.2); 3.79–3.87 m (0.85H, *cis, trans*-H^3); 4.83–4.99 m (1H, H^5), 10.86 s (0.15H, OH). The ^{19}F (δ, ppm): 37.80–38.10 m (2F, CF_2); 39.30–39.80 m (2F, CF_2); 49.60–53.00 m (2F, CH_2CF_2); 82.60–82.69 m (3F, CF_3). Found, %: C 36.47; H 2.47; F 47.20. $C_{11}H_9F_9O_3$. Calculated, %: C 36.68; H 2.52; F 47.47.

3-Ethoxycarbonyl-5-(2,2,3,3,4,4,4-heptafluorobutyl)tetrahydrofuran-2-one (III) was synthesized like the lactones **IIa–IIc** from compound **Ib** and malonic ester. Yield 28 %, white crystals, mp 28–29°C. The IR spectrum, ν, cm^{-1}: 1775, 1740 (C=O). The ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 1.29–1.35 m (3H, Me); 2.28 d.d.d (0.4H, *trans*-H^{4b}, *J* 13.3, 9.4, 8.3); 2.34–2.82 m

(3.2H, H^6, *cis*-H^4); 2.87 d.d.d (0.4H, *trans*-H4a, *J* 13.3, 6.5, 3.5); 3.64 d.d (0.4H, *trans*-H^3, *J* 9.4, 3.5); 3.70 d.d (0.6H, *cis*-H^3, *J* 10.5, 9.2); 4.22–4.32 m (2H, OCH_2), 4.87 d.d.d.d (0.6H, *cis*-H^5, *J* 9.1, 6.5, 6.4, 6.0); 5.06 d.d.d.d (0.4H, *trans*-H^5, *J* 8.3, 6.7, 6.5, 5.9). The ^{19}F (δ, ppm): 34.1–34.25 m (2F, CF_2); 48.17–48.45 m (2F, CH_2CF_2); 81.50–81.60 m (3F, CF_3). Found, %: C 38.73; H 3.25; F 39.42. $C_{11}H_{11}F_7O_4$. Calculated, %: C 38.84; H 3.26; F 39.09.

The X-ray structural investigation of compound **IIb** was carried out at the temperature t = 120(2) K on a Xcalibur 3 diffractometer with a CCD-detector, using SHELXL-97 program package [12]. Ther irradiadion wavelength λ = 0.71073 (MoK_a). Crystal size 0.43×0.31×0.09 mm, colorless plates, monoclinic, space group $P2_1/c$. A unit cell parameters: a = 25.992(4), b = 8.9660(10), c = 10.6142(13), β = 92.829(11). The experiment was completed at the angles θ ≤ 26.0° to 95.6%. The data collected included a set of 4829 independent reflexes, of them 2217 with $I > 2\sigma(I)$. The structure was solved by the direct method in an isotropic approximation and refined in anisotropic approximation for the non-hydrogen atoms. The hydrogen atoms were placed into geometrically calculated positions and included into refinement in isotropic approximation using the *rider* model. The correction for extinction was too small (μ = 0.187 mm^{-1}) and therefore omitted. The final values of divergence parameters are as follows: R_1 = 0.0686, wR_2 = 0.1501 [for $I > 2\sigma(I)$]. The maximal and minimal peaks of residual electron density are 0.344 and –0.329 e $Å^{-3}$.

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The crystallographic parameters of compound **IIb** are deposited completely in the Cambridge Structural Data Bank (CCDC XXXXXX) and are available at www.ccdc.cam.ac.uk/conts/retrieving.html (or CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk).

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