Chemistry of Heterocyclic Compounds, Vol. 36, No. 8, 2000

THERMAL REARRANGEMENT OF CONDENSED ALKOXY-SUBSTITUTED 2-TRIFLUOROMETHYL-4H-PYRAN-4-ONES TO SPIROANNELATED 3(2H)-FURANONES

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Isomerization of the acetates and benzoates of condensed hydroxy-substituted 2-trifluoromethyl-4H-pyran-4-ones at 300-320°C gave the corresponding derivatives of spiroannelated 3(2H)-furanones. Their structure was confirmed by spectral data and by X-ray crystallographic analysis.

Keywords: acyloxy group, 2,3-dihydro-4H-pyran-4-ones, spiro compounds, 3(2H)-furanones, X-ray crystallographic analysis, thermal rearrangement.

The participation of the neighboring to the reaction center acyloxy group in nucleophilic substitution, isomerization, and other transformations has been discussed widely in the literature and has been used for the solution of various synthetic problems (in particular in the chemistry of carbohydrates [1]), for the isomerization of monosaccharides [2, 3], for the synthesis of oligosaccharides [4, 5], and for the mutual transformation of the pyranose and furanose forms of carbohydrates and related systems [6, 7]. Such reactions are usually performed under mild conditions in the presence of electrophilic catalysts and involve the formation of acyloxonium ions [1]. In the present work the possibility for uncatalyzed thermal isomerization of the dihydropyranone system to the corresponding furan system, accompanied by migration of the acyloxy group, was studied.

2-Perfluoroalkyl-4H-pyran-4-ones, which are of interest as the precursors for substituted nitrogen-containing heterocyclic compounds [8, 9], can be obtained by dehydration of the corresponding 3-hydroxy-2,3-dihydro-4H-pyran-4-ones by the action of thionyl chloride in pyridine [10]. However, the 2,3-dialkyl-substituted hydroxydihydropyranones **1-3** are dehydrated with difficulty under these conditions, and this is due to the *cis* arrangement of the hydroxyl group and the vicinal hydrogen atom, which is unfavorable for elimination [11].

In the present work the pyrolysis of the acetates of condensed hydroxypyranones **4a, 5a** gives the spiro-annellated 3(2H)-furanones **6a** and **7** respectively with yields of 70 and 76% instead of the expected products from the *syn* elimination of acetic acid. The isomerization of the acetates **4a**, **5a** takes place during their single-stage distillation at atmospheric pressure and during external heating of the reaction mixture at 300-320°C. In addition to the products **6a**, **7a** the distillate contains 15-20% of the initial acetates **4a**, **5a**, but this mixture is probably not an equilibrium mixture, since the formation of the acetoxydihydropyranone **4a** is not observed as a result of distillation of the individual spiro compound **6a**. Treatment of the pyranone **4a** at the same temperature in a sealed tube in order to increase its conversion into the rearrangement product was accompanied by resinification of the reaction mass and did not lead to an increase in the yield of the furanone **6a**.

Belarus State University, Minsk; e-mail: tyvorskii@chem.bsu.unibel.by. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1028-1034, August, 2000. Original article submitted January 23, 1999.

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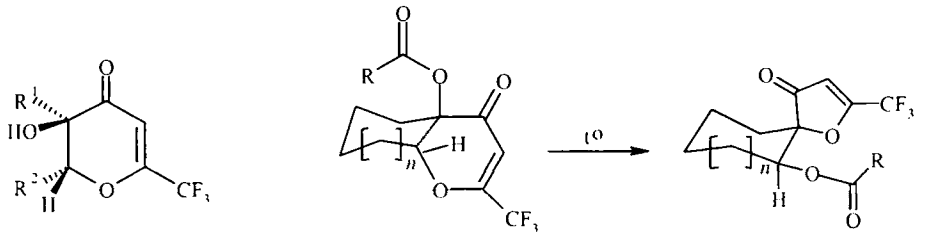


1—3 **4a,b; 5a** **6a,b; 7a**

1 $R^1 = R^2 = Me$; **2** $R^1R^2 = (CH_2)_4$; **3** $R^1R^2 = (CH_2)_5$;
4, **6** $n = 1$; **5**, **7** $n = 0$, **a** R = Me, **b** R = Ph

Similarly, the thermal rearrangement of benzoate **4b** led to the spiro compound **6b** with a 71% yield. The crude reaction product did not contain the initial pyranone **4b** as impurity, due probably to the possibility that the reaction mixture reaches a higher temperature. At the same time the isomerization in this case took place in a less well-defined manner and was accompanied by the formation of small amounts of unidentified compounds (up to 5%).

The structure of the obtained compounds **6a,b**, **7a** was confirmed by the results of elemental analysis and also by spectral data.

The main difference between the ^1H NMR spectra of the furanones **6a,b** and the spectra of the initial dihydropyranones **4a,b** is that the signal of the hydrogen atom of the CHOCOR fragment for compounds **6a,b** is a characteristic doublet of doublets with spin–spin coupling constants of 10.0-10.5 and 5.0 Hz, indicating the axial position of this atom in the cyclohexane ring. In the spectrum of the cyclopentane analog **7a** the signal of the H atom appears in the form of a multiplet with a width of 13 Hz, which favors a pseudoequatorial orientation of the acetoxyl group. In the ^{13}C NMR spectra of the spiro compounds **6a,b**, **7a** the signal of the carbon atom in the ketone carbonyl group is observed in the region of 201-203 ppm characteristic of 3(2H)-furanones [12], whereas in the case of the initial dihydropyranones it lies at 186-191 ppm [10]. In the IR spectra of the products **6a,b**, **7a**, in spite of conjugation with the C=C bond, the absorption band of the carbonyl group is observed in the region of 1720-1725 cm^{-1}, which is also typical of 3(2H)-furanones [13, 14].

The structure of the spiro compound **6a** was determined by X-ray crystallography. The obtained data make it possible to reach the following conclusions about the conformation and configuration of the molecule **6a** (Fig. 1). The furan ring is planar; the average deviation of the atoms forming the ring from the mean-square plane amounts to 0.002 Å.

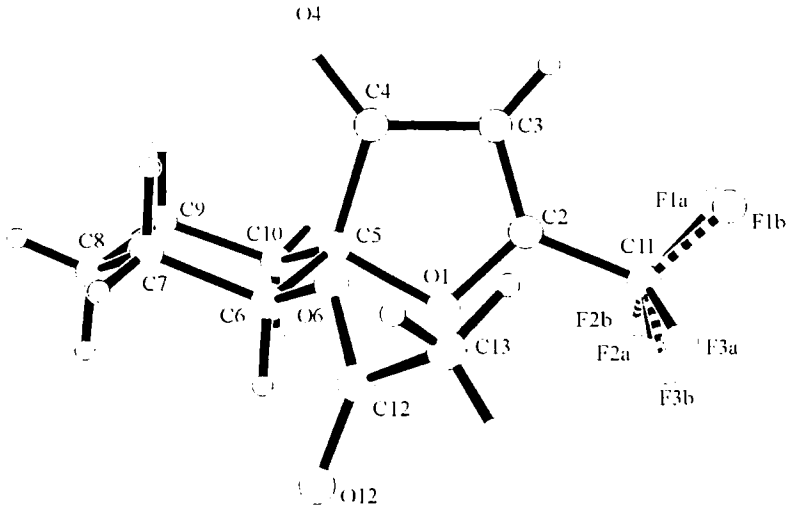


Fig. 1. The molecular structure of 6-acetoxy-2-trifluoromethyl-1-oxaspiro[4,5]dec-2-en-4-one (**6a**).

TABLE 1. The Bond Lengths (d) in the Molecule **6a**

Bond	d, Å	Bond	d, Å
$O_{(1)}$–$C_{(2)}$	1.350(3)	$C_{(8)}$–$C_{(9)}$	1.516(5)
$O_{(1)}$–$C_{(5)}$	1.468(3)	$C_{(9)}$–$C_{(10)}$	1.532(5)
$C_{(2)}$–$C_{(3)}$	1.323(4)	$C_{(12)}$–$O_{(12)}$	1.191(3)
$C_{(2)}$–$C_{(11)}$	1.481(5)	$C_{(12)}$–$O_{(6)}$	1.339(3)
$C_{(3)}$–$C_{(4)}$	1.446(4)	$C_{(12)}$–$C_{(13)}$	1.487(4)
$C_{(4)}$–$O_{(4)}$	1.215(3)	$F_{(1a)}$–$C_{(11)}$	1.28(1)
$C_{(4)}$–$C_{(5)}$	1.534(3)	$F_{(2a)}$–$C_{(11)}$	1.22(1)
$C_{(5)}$–$C_{(6)}$	1.514(3)	$F_{(3a)}$–$C_{(11)}$	1.45(2)
$C_{(5)}$–$C_{(10)}$	1.520(3)	$F_{(1b)}$–$C_{(11)}$	1.35(2)
$C_{(6)}$–$O_{(6)}$	1.441(3)	$F_{(2b)}$–$C_{(11)}$	1.43(2)
$C_{(6)}$–$C_{(7)}$	1.508(3)	$F_{(3b)}$–$C_{(11)}$	1.21(2)
$C_{(7)}$–$C_{(8)}$	1.504(4)		

The trifluoromethyl group is disordered in the structure at two positions, rotated in relation to each other by an angle of ~25°. The cyclohexane ring has the chair conformation (torsion angles close to 60°). The acetoxyl substituent at the $C_{(6)}$ atom of the cyclohexane ring is in the equatorial position. The bond lengths and bond angles in the molecule **6a** (Tables 1, 2) are normal [15]. Some shortening of the C–F bond lengths in the disordered CF_3 group is due to its considerable librational movements. No shortened contacts are observed in the structure, and the packing of the molecules is therefore determined by van der Waals interactions.

It can be supposed on the basis of the data for the spiro compound **6a** that the isomerization of the dihydropyranones **4a,c**, **5a** involves participation of the acyloxy group, which attacks the neighboring bridgehead carbon atom from the rear side in relation to the cyclic oxygen atom. This is promoted by the fixed *trans*-diaxial arrangement of these groups in the initial pyranones **4a,b**, **5a**. The participation of the acyloxy group in the rearrangement process is also demonstrated indirectly by the fact that the unacylated hydroxypyranone **2** does not undergo the transformation when heated at 300-320°C.

TABLE 2. The Bond Angles (ω) in the Molecule **6a**

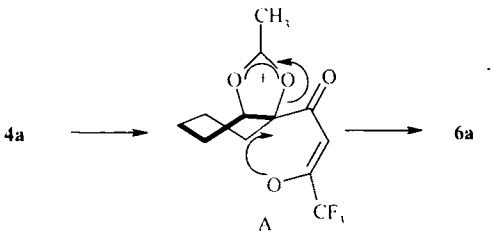
Angle	ω, deg.	Angle	ω, deg.
$C_{(2)}$–$O_{(1)}$–$C_{(5)}$	106.9(2)	$C_{(8)}$–$C_{(9)}$–$C_{(10)}$	112.5(2)
$C_{(3)}$–$C_{(2)}$–$O_{(1)}$	116.9(3)	$C_{(5)}$–$C_{(10)}$–$C_{(9)}$	111.1(2)
$C_{(3)}$–$C_{(2)}$–$C_{(11)}$	129.9(3)	$O_{(12)}$–$C_{(12)}$–$O_{(6)}$	123.3(2)
$O_{(1)}$–$C_{(2)}$–$C_{(11)}$	113.3(3)	$O_{(12)}$–$C_{(12)}$–$C_{(13)}$	125.4(2)
$C_{(2)}$–$C_{(3)}$–$C_{(4)}$	106.7(2)	$O_{(6)}$–$C_{(12)}$–$C_{(13)}$	111.3(2)
$O_{(4)}$–$C_{(4)}$–$C_{(3)}$	128.7(2)	$C_{(12)}$–$O_{(6)}$–$C_{(6)}$	118.3(2)
$O_{(4)}$–$C_{(4)}$–$C_{(5)}$	125.0(2)	$F_{(1a)}$–$C_{(11)}$–$F_{(2a)}$	106(1)
$C_{(3)}$–$C_{(4)}$–$C_{(5)}$	106.3(2)	$F_{(1a)}$–$C_{(11)}$–$F_{(3a)}$	110(1)
$O_{(1)}$–$C_{(5)}$–$C_{(6)}$	107.3(2)	$F_{(2a)}$–$C_{(11)}$–$F_{(3a)}$	106(1)
$O_{(1)}$–$C_{(5)}$–$C_{(10)}$	108.2(2)	$F_{(1a)}$–$C_{(11)}$–$C_{(2)}$	110.2(9)
$C_{(6)}$–$C_{(5)}$–$C_{(10)}$	109.8(2)	$F_{(2a)}$–$C_{(11)}$–$C_{(2)}$	119.0(9)
$O_{(1)}$–$C_{(5)}$–$C_{(4)}$	103.3(2)	$F_{(3a)}$–$C_{(11)}$–$C_{(2)}$	106(1)
$C_{(6)}$–$C_{(5)}$–$C_{(4)}$	114.1(2)	$F_{(1b)}$–$C_{(11)}$–$F_{(2b)}$	117(2)
$C_{(10)}$–$C_{(5)}$–$C_{(4)}$	113.7(2)	$F_{(1b)}$–$C_{(11)}$–$F_{(3b)}$	107(2)
$O_{(6)}$–$C_{(6)}$–$C_{(7)}$	110.3(2)	$F_{(2b)}$–$C_{(11)}$–$F_{(3b)}$	102(1)
$O_{(6)}$–$C_{(6)}$–$C_{(5)}$	106.8(2)	$F_{(1b)}$–$C_{(11)}$–$C_{(2)}$	112(1)
$C_{(7)}$–$C_{(6)}$–$C_{(5)}$	112.7(2)	$F_{(2b)}$–$C_{(11)}$–$C_{(2)}$	104.8(9)
$C_{(8)}$–$C_{(7)}$–$C_{(6)}$	109.5(2)	$F_{(3b)}$–$C_{(11)}$–$C_{(2)}$	115.0(9)
$C_{(9)}$–$C_{(8)}$–$C_{(7)}$	110.5(2)		

TABLE 3. The Coordinates (x/a, y/b, z/c, Å × 10^4) and Equivalent Isotropic Temperature Parameters [$U(eq)$, Å^2 × 10^3] of the Atoms in Structure **6a**

Atom	x/a	y/b	z/c	$U(eq)$
$O_{(1)}$	712(1)	4645(3)	1316(1)	72(1)
$C_{(2)}$	98(1)	3622(5)	1077(1)	78(1)
$C_{(3)}$	108(2)	2203(5)	646(1)	78(1)
$C_{(4)}$	822(1)	2173(4)	560(1)	62(1)
$C_{(5)}$	1240(1)	3821(4)	1004(1)	58(1)
$C_{(6)}$	1823(1)	2729(4)	1447(1)	54(1)
$C_{(7)}$	2437(1)	2001(5)	1193(1)	74(1)
$C_{(8)}$	2739(2)	4016(6)	945(1)	96(1)
$C_{(9)}$	2177(2)	5169(6)	494(2)	108(1)
$C_{(10)}$	1531(2)	5832(4)	732(1)	88(1)
$C_{(12)}$	1614(1)	596(4)	2252(1)	64(1)
$C_{(13)}$	1220(2)	-1367(5)	2412(1)	91(1)
$O_{(1)}$	1063(1)	1116(3)	206(1)	79(1)
$O_{(6)}$	1517(1)	811(3)	1676(1)	62(1)
$O_{(12)}$	1978(1)	1829(4)	2586(1)	101(1)
$F_{(1a)}$*	-1081(6)	3760(30)	1014(9)	153(5)
$F_{(2a)}$*	-553(5)	6310(30)	1459(12)	180(7)
$F_{(3a)}$*	-402(9)	3110(60)	1884(8)	206(7)
$F_{(1b)}$*^{2}	-1072(10)	3040(60)	1151(15)	201(11)
$F_{(2b)}$*^{2}	-569(9)	6680(30)	1229(11)	180(7)
$F_{(3b)}$*^{2}	-373(10)	4270(50)	1864(7)	142(6)
$C_{(11)}$	-494(2)	4323(11)	1341(3)	125(2)

* Population of position 0.58(4).

*^{2} Population of position 0.42(4).



Probably as in the case of similar catalytic processes [6, 7], the reaction proceeds through the formation of the type **A** acyloxonium ions. However, additional experiments are required to confirm this idea.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer at 200 and 50.3 MHz respectively for solutions in deuterochloroform. The chemical shifts were measured with reference to TMS. The IR spectra were recorded on a Specord 75 IR spectrophotometer in carbon tetrachloride. The reactions and the purity of the products were monitored by TLC on Silufol UV-254 plates with development in iodine vapor or with aqueous potassium permanganate solution.

X-ray Crystallographic Investigation of Compound 6a. Crystals of furanone **6a** were obtained by crystallization from hexane. X-ray crystallographic analysis was carried out on a prismatic crystal (0.66×0.45×0.32 mm), sealed into a glass capillary (on account of the instability of the compound in the X-ray beam). A three-dimensional set of X-ray diffraction data was collected on an automatic four-circle Nicolet R3m

diffractometer with MoKα radiation, a graphite monochromator, and a θ/2θ scan ($2\theta_{max}$ = 55°). The total number of measured reflections was 3276, and the number of unique reflections was 3074 ($R_{(int)}$ = 0.0103). The compound crystallizes in the monoclinic syngony with space group *C*2/*c*. Unit cell parameters: *a* = 19.432(6); *b* = 5.935(1); *c* = 23.598(5) Å; β = 102.27(2)°; *V* = 2659(1) Å^3; *Z* = 8; $d_{X\text{-ray}}$ = 1.390 g/cm^3; μ = 1.3 cm^{-1}. The structure of the compound was interpreted by the direct method. The hydrogen atoms were localized from a Fourier difference synthesis. The structure was refined by full-matrix least-squares treatment including the anisotropy of the thermal vibrations of the non-hydrogen atoms. The final values of the divergence factors were: R^1 = 0.0626, wR^2 = 0.1701 ($I > 2\sigma(I)$); R^1 = 0.1085, wR^2 = 0.2044 (all data); goodness of fit (GOOF) 0.997. Absorption was not taken into account. All the calculations were carried out with the SHELX-97 software (PC version) [16-18]. The coordinates and the equivalent isotropic temperature parameters of the atoms are give in Table 3.

4a-Hydroxy-2-trifluoromethyl-4a,5,6,7,8,8a-hexahydro-4H-1-benzopyran-4-one (2) and Its Acetate 4a. The compounds were obtained by the method [11]. ^{13}C NMR spectrum of compound **4a**, ppm: 190.59 (C=O); 169.44 (<u>C</u>OCH$_3$); 157.92 (q, $^2J_{C\text{-}F}$ = 37 Hz, <u>C</u>CF$_3$); 118.67 (q, $^1J_{C\text{-}F}$ = 275 Hz, CF$_3$); 103.33 (q, $^3J_{C\text{-}F}$ = 3 Hz, <u>C</u>H=CCF$_3$); 78.15 (CH–O); 77.93 (<u>C</u>–OCOCH$_3$); 29.28 (CH$_2$); 25.59 (CH$_2$); 20.93 (CO<u>C</u>H$_3$); 19.35 (CH$_2$); 18.96 (CH$_2$).

4a-Hydroxy-2-trifluoromethyl-5,6,7,7a-tetrahydrocyclopenta[*b*]pyran-4(4aH)-one (3). The compound was obtained by the condensation of 1-acetyl-1,2-epoxycyclopentane [19] with ethyl trifluoroacetate by the method [11]. Yield 68%; mp 67°C (hexane). IR spectrum, cm^{-1}: 1645 (C=C), 1700 (C=O), 3495 (O–H). ^{1}H NMR spectrum, ppm: 5.86 (1H, s, CH=C); 4.81-4.74 (1H, m, CH–O); 3.60 (1H, br. s, OH); 2.46-1.76 (6H, m, CH$_2$). Found, %: C 48.89; H 4.27. $C_9H_9F_3O_3$. Calculated, %: C 48.66; H 4.08.

4a-Acetoxy-2-trifluoromethyl-5,6,7,7a-tetrahydrocyclopenta[*b*]pyran-4(4aH)-one (5a). The compound was obtained by the acylation of compound **3** with an excess of acetyl chloride by the known procedure [11]. Yield 87%; mp 49-50°C (pentane). IR spectrum, cm^{-1}: 1650 (C=C), 1705 (C=O), 1755 (C=O). ^{1}H NMR spectrum, ppm: 5.85 (1H, s, CH=C); 5.31-5.24 (1H, m, CH–O); 2.10 (3H, s, CH$_3$CO); 2.28-1.92 (6H, m, CH$_2$). ^{13}C NMR spectrum, ppm: 188.89 (C=O); 169.73 (<u>C</u>OCH$_3$); 156.67 (q, $^2J_{C\text{-}F}$ = 3 Hz, <u>C</u>H=CCF$_3$); 118.64 (q, $J_{C\text{-}F}$ = 275 Hz, CF$_3$); 102.03 (q, $^3J_{C\text{-}F}$ = 3 Hz, <u>C</u>H=CCF$_3$); 87.64 (CH–O); 86.20 (<u>C</u>–OCOCH$_3$); 34.07 (CH$_2$); 31.10 (CH$_2$); 21.16 (CH$_2$); 20.79 (CO<u>C</u>H$_3$). Found, %: C 50.23; H 4.39. $C_{11}H_{11}F_3O_4$. Calculated, %: C 50.01; H 4.20.

4a-Benzoyloxy-2-trifluoromethyl-4a,5,6,7,8,8a-hexahydro-4H-1-benzopyran-4-one (4b). The compound was obtained by the benzoylation of hydroxypyranone **2** (1.1 g, 4.7 mmol) in pyridine (2.7 ml) using benzoyl chloride (0.85 ml, 7.1 mmol). Benzoate **4b** (1.56 g, 97%) was obtained; mp 128-128.5°C (hexane). IR spectrum, cm^{-1}: 1650 (C=C), 1705 (C=O), 1735 (C=O). ^{1}H NMR spectrum, ppm: 8.12-7.98 (2H, m, Ph); 7.67-7.34 (3H, m, Ph); 5.95 (1H, s, CH=C); 5.46-5.36 (1H, m, CH–O); 2.18-1.41 (8H, m, CH$_2$). ^{13}C NMR spectrum, δ, ppm: 190.41 (C=O); 164.68 (<u>C</u>OPh); 158.01 (q, $^2J_{C\text{-}F}$ = 37 Hz, <u>C</u>CF$_3$); 133.76 (C, Ph), 130.02 (2C, Ph); 129.18 (C$_{quat}$, Ph); 128.59 (2C, Ph); 118.73 (q, $^1J_{C\text{-}F}$ = 275 Hz, CF$_3$); 103.47 (q, $^3J_{C\text{-}F}$ = 3 Hz, <u>C</u>H=CCF$_3$); 78.31 (CH–O); 78.19 (<u>C</u>–OCOPh); 29.45 (CH$_2$); 25.71 (CH$_2$); 19.73 (CH$_2$); 19.06 (CH$_2$). Found, %: C 60.23; H 4.67. $C_{17}H_{15}F_3O_4$. Calculated, %: C 60.00; H 4.44.

6-Acetoxy-2-trifluoromethyl-1-oxaspiro[4.5]dec-2-en-4-one (6a). A sample of compound **4a** (2.3 g, 8.2 mol) was kept in a distillation flask at 745 mm Hg and a bath temperature of 300-320°C. The distillate boiling at 230-245°C was collected, and the spiro compound **6a** (1.58 g, 70%) was obtained from it by crystallization from hexane; mp 75-76°C. IR spectrum, cm^{-1}: 1640 (C=C), 1725 (C=O), 1755 (C=O). ^{1}H NMR spectrum, ppm: 5.96 (1H, s, CH=C); 5.13 (1H, dd, *J* = 10.0; 5.0 Hz, CH–O); 2.01 (3H, s, CH$_3$CO); 2.21-1.18 (8H, m, CH$_2$). ^{13}C NMR spectrum, ppm: 202.62 (C=O); 173.09 (q, $^2J_{C\text{-}F}$ = 41 Hz, CCF$_3$); 170.44 (<u>C</u>OCH$_3$); 118.51 (q, $^1J_{C\text{-}F}$ = 273 Hz, CF$_3$); 106.44 (<u>C</u>H=CCF$_3$); 91.53 (C-O); 73.68 (<u>C</u>H-OCOCH$_3$); 31.38 (CH$_2$); 26.81 (CH$_2$); 23.03 (CH$_2$); 21.26 (CO<u>C</u>H$_3$); 20.14 (CH$_2$). Found, %: C 51.98; H 4.92. $C_{12}H_{13}F_3O_4$. Calculated, %: C 51.80; H 4.71.

6-Acetoxy-2-trifluoromethyl-1-oxaspiro[4,4]non-2-en-4-one (7a). The compound was obtained similarly to compound **6a** by distilling of compound **5a** (1.72 g, 6.5 mmol). The distillate boiling at 215-230°C was collected and chromatographed on a column of silica gel with 1:1 mixture of cyclohexane and ether as eluant. Furanone **7a** (1.0 g, 76%) and the initial pyranone **5a** (0.4 g) were isolated. Spiro compound **7a**: mp 33-34°C (pentane). IR spectrum, cm^{-1}: 1635 (C=C), 1725 (C=O), 1750 (C=O). ^{1}H NMR spectrum, ppm: 6.03 (1H, s, CH=C); 5.25-5.17 (1H, m, CH–O); 2.04 (3H, s, CH$_3$CO); 2.39-1.88 (6H, m, CH$_2$). ^{13}C NMR spectrum, ppm:

200.65 (C=O); 172.06 (q, $^2J_{C-F}$ = 40 Hz, $\underline{C}CF_3$); 170.30 ($\underline{C}OCH_3$); 118.08 (q, $^1J_{C-F}$ = 273 Hz, CF_3); 106.45 ($\underline{C}H{=}CCF_3$); 98.03 (C–O); 79.40 ($\underline{C}H{-}OCOCH_3$); 34.16 (CH_2); 31.12 (CH_2); 21.91 (CH_2); 20.71 ($CO\underline{C}H_3$). Found, %: C 50.25; H 4.43. $C_{11}H_{11}F_3O_4$. Calculated, %: C 50.01; H 4.20.

6-Benzoyloxy-2-trifluoromethyl-1-oxaspiro[4,5]dec-2-en-4-one (6b). A sample of compound **4b** (0.50 g, 0.15 mmol) was kept at 300-320°C for 15 min. The cooled reaction mass was extracted with boiling chloroform (10 ml). The residue after removal of the solvent was chromatographed on a column of silica gel with a 3:1 mixture of hexane and ether as eluant. Furanone **6b** (0.36 g, 71%) was isolated in the form of an oil. IR spectrum, cm^{-1}: 1720 (C=O). ^1H NMR spectrum, ppm: 7.97-7.86 (2H, m, Ph); 6.03 (1H, s, CH=C); 5.38 (1H, dd, J = 10.5; 5.0 Hz, CH–O); 2.38-1.41 (8H, m, CH_2). ^{13}C NMR spectrum, ppm: 202.01 (C=O); 172.79 (q, $^2J_{C-F}$ = 41 Hz, $\underline{C}CF_3$); 165.34 ($\underline{C}OPh$); 133.33 (C, Ph); 129.62 (2C, Ph); 129.45 (C_{quat}, Ph); 128.47 (2C, Ph); 117.81 (q, $^1J_{C-F}$ = 273 Hz, CF_3); 105.68 ($\underline{C}H{=}CCF_3$); 91.19 (C–O); 73.88 ($\underline{C}H{-}OCOPh$); 30.99 (CH_2); 26.30 (CH_2); 22.57 (CH_2); 19.58 (CH_2). Found, %: C 60.25; H 4.63. $C_{17}H_{15}F_3O_4$. Calculated, %: C 60.00; H 4.44.

The authors express their gratitude to the Russian Fundamental Research Fund for financial assistance in payment for the license for the use of the Cambridge structural data bank (Project 96-07-89187) during analysis of the results obtained in the present work.

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