Letters to the Editor

Formation of fluoroalkyl-containing pyran-4-one in the reaction of lithium 4,4,4-trifluoro-1-phenylbutane-1,3-dionate with oxalyl chloride

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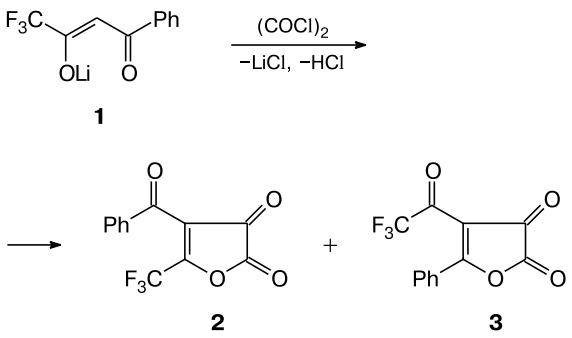
Cyclization of 1,3-dicarbonyl compounds with oxalyl chloride is the most commonly used preparative procedure for the construction of furan-2,3-diones.[1] Monofluoroalkyl-containing 1,3-diketones and 1,3-keto esters are known to react with oxalyl chloride exclusively at the fluoroacyl substituent to form 3,5-dihydroxyfuran-2-ones.[2] We demonstrated that the reaction of lithium 4,4,4-trifluoro-1-phenylbutane-1,3-dionate **1** with oxalyl chloride involves a series of transformations (Schemes 1 and 2) giving rise to 3-benzoyl-5-(2,2,2-trifluoroacetyl)-2-(trifluoromethyl)-6-phenylpyran-4(4*H*)-one (**6**). The structure of compound **6** was established by X-ray diffraction (Fig. 1).

The first reaction step can produce regioisomeric furandiones **2** and/or **3** (see Scheme 1), whose thermal decarbonylation affords the same ketene **4** (see Scheme 2).

Scheme 1



The formation of pyran-4-one **6** can occur by two pathways. On the one hand, ketene **4** can attack 1,3-diketone molecule **5**, which is derived from compound **1**

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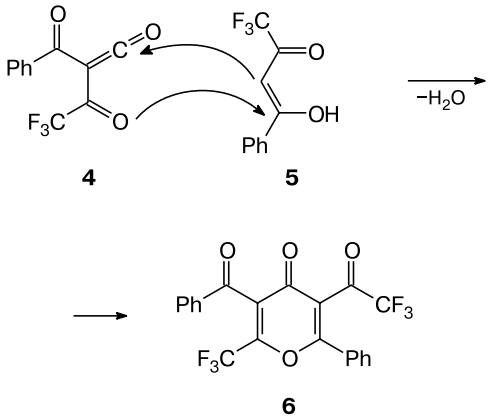
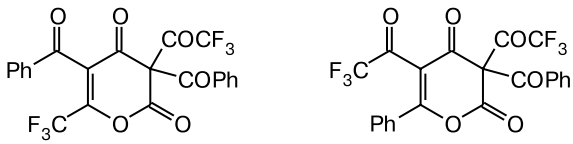
Scheme 2



under the action of HCl released in the reaction (see Scheme 2).

On the other hand, ketene **4** can undergo dimerization to form unstable dihydropyrandiones **7** and/or **8**.



Subsequent decarboxylation of one of the dimers (**7**) also can afford pyrone **6** by analogy with the known reaction of the dibenzoylketene dimer.[3]

The molecular structure of compound **6** is shown in Fig. 1. The final bond lengths and bond angles are given in Table 1.

In molecule **6**, the dihedral angles between the plane of the pyran ring and the planes of the phenyl groups are 52.8 and 87.3°. The principal geometric parameters of molecule **6** agree well with those typical of pyran systems.[4]

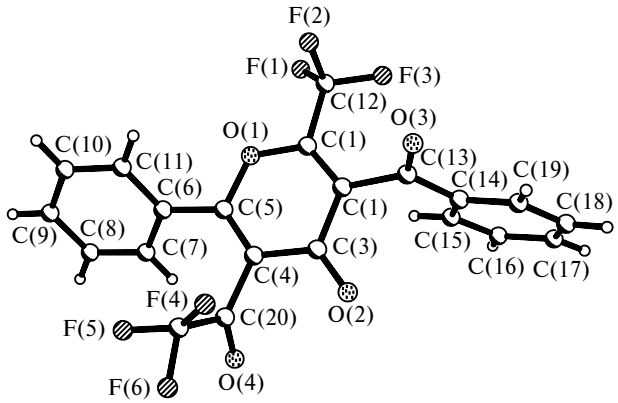


Fig. 1. Molecular structure of compound **6**.

The synthesis of **1** was described in the study.[5] The course of the reactions was monitored by TLC on Silufol UV-254 plates with the use of $CHCl_3$ as the eluent. The plates were visualized with aqueous solutions of copper acetate and $KMnO_4$ and using iodine vapor. The NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz for ^1H and 376 MHz for ^{19}F) in $CDCl_3$, with Me_4Si and C_6F_6 as the internal standards for ^1H and ^{19}F, respectively. The IR spectra were measured on a Spectrum One Fourier-transform IR spectrometer (Perkin Elmer) in Nujol mulls. The mass spectra were obtained on a MAT INCOS-50 spectrometer (the ionizing electron energy was 70 eV) using a direct inlet system.

3-Benzoyl-5-trifluoroacetyl-2-trifluoromethyl-6-phenylpyran-4(4*H*)-one (6). A solution of diketonate **1** (1 g, 4.5 mmol) and oxalyl chloride (0.4 mL, 4.5 mmol) in anhydrous toluene (25 mL) was refluxed for 3 h. After completion of the reaction, the precipitate was filtered, and the filtrate was concentrated and cooled. The precipitate that formed was filtered off and recrystallized from diethyl ether. Compound **6** was obtained in a yield of 0.33 g (34%), m.p. 167—169 °C. Found (%): C, 56.71; H, 2.36; F, 26.00. $C_{21}H_{10}F_6O_4$. Calculated (%): C, 57.28; H, 2.29; F, 25.88. IR, ν/cm^{-1}: 1750, 1670, 1660 (CO). ^1H NMR, δ: 7.49—7.90 (m, Ph). ^{19}F NMR, δ: 85.41 (s, CF_3); 94.83 (s, $COCF_3$). MS, *m/z* (I_{rel} (%)): 440 $[M]^+$ (14), 411 (36), 371

Table 1. Selected bond lengths (*d*) and bond angles (ω) in compound **6**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
O(1)—C(1)	1.355(4)	C(1)—O(1)—C(5)	119.2(2)	C(5)—C(4)—C(20)	122.3(3)
O(1)—C(5)	1.367(4)	C(2)—C(1)—O(1)	124.4(3)	C(3)—C(4)—C(20)	115.9(2)
O(2)—C(3)	1.213(4)	C(2)—C(1)—C(12)	126.6(3)	C(4)—C(5)—O(1)	120.9(3)
O(3)—C(13)	1.209(4)	O(1)—C(1)—C(12)	109.0(3)	C(4)—C(5)—C(6)	127.4(3)
O(4)—C(20)	1.185(4)	C(1)—C(2)—C(3)	119.3(3)	O(1)—C(5)—C(6)	111.7(2)
C(1)—C(2)	1.328(4)	C(1)—C(2)—C(13)	124.1(3)	O(3)—C(13)—C(14)	123.2(3)
C(1)—C(12)	1.510(5)	C(3)—C(2)—C(13)	116.3(3)	O(3)—C(13)—C(2)	117.4(3)
C(2)—C(3)	1.471(4)	O(2)—C(3)—C(4)	123.2(3)	C(14)—C(13)—C(2)	119.3(3)
C(2)—C(13)	1.516(4)	O(2)—C(3)—C(2)	122.6(3)	O(4)—C(20)—C(4)	124.9(3)
C(3)—C(4)	1.451(4)	C(4)—C(3)—C(2)	114.2(2)	O(4)—C(20)—C(21)	117.8(3)
C(4)—C(5)	1.348(4)	C(5)—C(4)—C(3)	121.9(3)	C(4)—C(20)—C(21)	117.3(3)
C(4)—C(20)	1.494(4)				
C(5)—C(6)	1.464(4)				
C(20)—C(21)	1.543(6)				

$[M - CF_3]^+$ (24), 343 $[M - COCF_3]^+$ (6), 129 (26), 105 $[COPh]^+$ (100), 77 $[Ph]^+$ (57), 69 $[CF_3]^+$ (6).

X-ray diffraction study was carried out on an Enraf Nonius CAD-4 diffractometer (λ-Mo, graphite monochromator, 293 K, ω-scanning technique, $2\theta_{max} = 50.2°$). A total of 3502 reflections were collected, of which 3384 reflections were independent. The structure was solved by direct methods using the SHELXS97 program package[6] and refined anisotropically by the least-square method with the use of the SHELXL97 program package[7] to $R_1 = 0.0660$, $wR_2 = 0.1893$ for 2028 reflections with $F^2 > 2\sigma F^2$. The fluorine atoms of the trifluoromethyl groups are disordered; each atom occupies two equivalent positions with occupancies of ~0.6 and ~0.4.

Crystals of 3-benzoyl-5-trifluoroacetyl-2-trifluoromethyl-6-phenylpyran-4(4*H*)-one (**6**) are triclinic. At 293 K, a = 10.169 (4) Å, b = 10.454 (5) Å, c = 10.814 (7) Å, $\alpha = 85.73(4)°$, $\beta = 63.71$ (4)°, $\gamma = 70.20(4)°$, V 965.9 (9) Å^3, $Z = 2$, d_{calc} = 1.514 g cm^{-3}, space group $P\bar{1}$.

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