Russian Chemical Bulletin, International Edition, Vol. 50, No. 1, pp. 101—103, January, 2001 101

Unexpected reaction of 1,1,1,10,10,10-hexafluorodecane-2,4,7,9-tetrone with methyl trifluoroacetate

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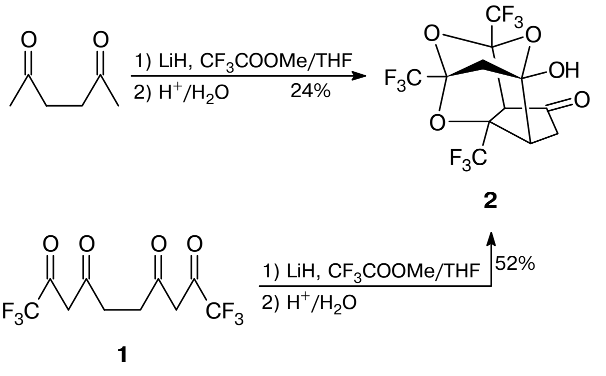
Hexane-2,5-dione or 1,1,1,10,10,10-hexafluorodecane-2,4,7,9-tetrone react with methyl trifluoroacetate in the presence of LiH to give, upon treatment with diluted acid, 6-hydroxy-9-oxo-2,4,10-tris(trifluoromethyl)-3,11,12-trioxatetracyclo[5,2,1,$0^{2,6}$,$0^{4,10}$]dodecane. The structure of this compound was determined by X-ray diffraction study.

Key words: hexane-2,5-dione, 1,1,1,10,10,10-hexafluorodecane-2,4,7,9-tetrone, methyl trifluoroacetate, condensation; 6-hydroxy-9-oxo-2,4,10-tris(trifluoromethyl)-3,11,12-trioxatetracyclo[5,2,1,$0^{2,6}$,$0^{4,10}$]dodecane, X-ray diffraction analysis.

Bis(β-diketones) are attractive chelating compounds that allow one to obtain oligomeric metal chelates,[1] intermediate products for the synthesis of heterocycles,[2] and possible comonomers.[3] Being difficult to synthesize, they are poorly studied. There are only a few published communications reporting the synthesis of bis(β-diketones) with aromatic,[1,4] aliphatic,[4,5] and polyfluoroaliphatic[6] fragments between the β-dicarbonyl pentads.

Previously,[7] bis(β-diketone) **1** with the terminal CF_3 groups was synthesized by the reaction of acetonylacetone with methyl trifluoroacetate. An attempt to optimize the reaction conditions unexpectedly yielded an unknown compound **2**, instead of bis(β-diketone) **1** (Scheme 1). Believing that this product results from the reaction of methyl trifluoroacetate with the bis(β-diketone) formed, we carried out the reaction of tetraketone **1** with methyl trifluoroacetate and found the reaction product to be the same compound **2**.

Scheme 1



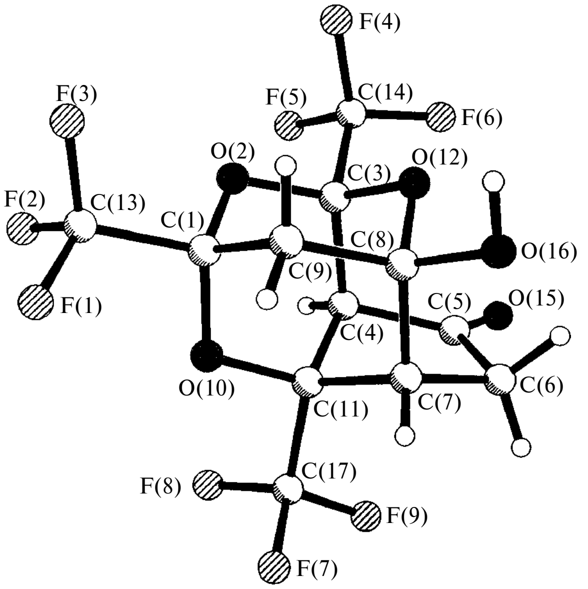


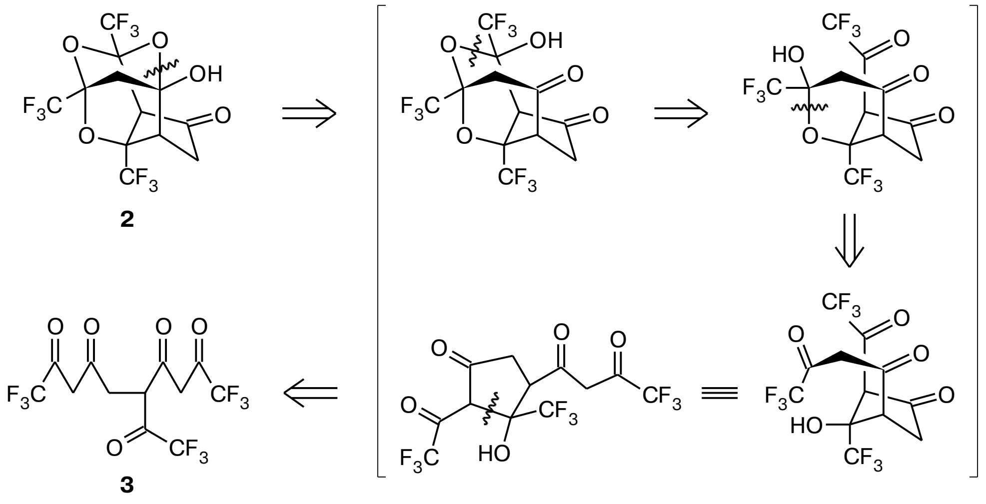
Fig. 1. Molecular structure of compound **2**.

The structure of compound **2** (Fig. 1) was proved by X-ray diffraction analysis. Bond lengths and angles in structure **2** (Tables 1, 2) are standard.[8]

The crystal has a bladed molecular packing. The stacks of molecules along the Y axis are united by the 2_1 axis into columns arranged in layers along the X axis. The molecules in the stacks are held together by intermolecular O(16)—H...O(15) hydrogen bonds ($1.5-x$, $0.5+y$, $0.5-z$) (O...O 2.792(4) Å, H...O 1.95(4) Å, and the O—H...O angle 171(3)°).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 98—100, January, 2001.

Scheme 2



Retrosynthetic analysis of compound **2** (Scheme 2) suggests that bis(β-diketone) initially condenses with methyl trifluoroacetate to give pentacarbonyl compound **3**, as in analogous transformations of 1,3-diketones into 1,3,5-triketones.[9] Subsequent treatment of the reaction mixture with an aqueous solution of an acid causes compound **3** to undergo a series of successive intramolecular (aldol and then ketal) cyclizations that can result in compound **2**. The possible intermediates, including **3**, failed to be isolated.

Experimental

^{19}F NMR spectrum was recorded on a Tesla-BS-587A spectrometer (75.3 MHz) with hexafluorobenzene as the internal standard. IR spectrum was recorded on a Specord IR-75 instrument (Vaseline oil).

Table 1. Bond lengths in structure **2**

Bond	d/Å	Bond	d/Å
F(1)—C(13)	1.332(4)	C(3)—C(14)	1.534(4)
F(2)—C(13)	1.329(4)	C(3)—C(4)	1.556(4)
F(3)—C(13)	1.320(4)	C(4)—C(5)	1.527(4)
F(4)—C(14)	1.323(4)	C(4)—C(11)	1.544(4)
F(5)—C(14)	1.327(4)	C(5)—O(15)	1.208(4)
F(6)—C(14)	1.321(4)	C(5)—C(6)	1.512(4)
F(7)—C(17)	1.324(4)	C(6)—C(7)	1.529(4)
F(8)—C(17)	1.316(4)	C(7)—C(8)	1.531(4)
F(9)—C(17)	1.338(4)	C(7)—C(11)	1.544(4)
C(1)—O(10)	1.409(3)	C(8)—O(16)	1.371(3)
C(1)—O(2)	1.419(3)	C(8)—O(12)	1.479(3)
C(1)—C(13)	1.517(4)	C(8)—C(9)	1.514(4)
C(1)—C(9)	1.528(4)	O(10)—C(11)	1.419(3)
O(2)—C(3)	1.407(3)	C(11)—C(17)	1.535(4)
C(3)—O(12)	1.403(3)		

The crystals are monoclinic, space group $C2/c$, at $T = 20$ °C a = 13.710(5), b = 9.687(3), c = 20.717(7) Å, β = 91.01(3)°, $V = 2751(2)$ Å^3, $Z = 8$, $d_{\text{calc}} = 1.942$ g cm^{-3}.

The unit cell parameters and the intensities of 2433 reflections were measured on a Siemens P3/PC automated four-circle diffractometer ($T = 20$ °C, λMo-Kα radiation, graphite monochromator, θ/2θ scanning technique, $\theta_{\text{max}} = 25°$). The structure was solved by the direct method and refined by full-matrix

Table 2. Bond angles in structure **2**

Angle	ω/deg	Angle	ω/deg
O(10)—C(1)—O(2)	109.8(2)	C(9)—C(8)—C(7)	111.8(2)
O(10)—C(1)—C(13)	106.2(2)	C(8)—C(9)—C(1)	106.7(2)
O(2)—C(1)—C(13)	106.1(2)	C(1)—O(10)—C(11)	112.2(2)
O(10)—C(1)—C(9)	109.5(2)	O(10)—C(11)—C(17)	102.5(2)
O(2)—C(1)—C(9)	111.0(2)	O(10)—C(11)—C(4)	113.4(2)
C(13)—C(1)—C(9)	114.0(2)	C(17)—C(11)—C(4)	112.0(2)
C(3)—O(2)—C(1)	111.0(2)	O(10)—C(11)—C(7)	114.5(2)
O(12)—C(3)—O(2)	111.5(2)	C(17)—C(11)—C(7)	114.7(2)
O(12)—C(3)—C(14)	106.9(2)	C(4)—C(11)—C(7)	100.2(2)
O(2)—C(3)—C(14)	104.7(2)	C(3)—O(12)—C(8)	111.3(2)
O(12)—C(3)—C(4)	109.3(2)	F(3)—C(13)—F(2)	107.7(3)
O(2)—C(3)—C(4)	111.0(2)	F(3)—C(13)—F(1)	108.0(3)
C(14)—C(3)—C(4)	113.4(2)	F(2)—C(13)—F(1)	107.9(3)
C(5)—C(4)—C(11)	102.3(2)	F(3)—C(13)—C(1)	112.5(3)
C(5)—C(4)—C(3)	108.6(2)	F(2)—C(13)—C(1)	110.5(3)
C(11)—C(4)—C(3)	103.9(2)	F(1)—C(13)—C(1)	110.1(3)
O(15)—C(5)—C(6)	126.5(3)	F(6)—C(14)—F(4)	108.2(3)
O(15)—C(5)—C(4)	125.0(3)	F(6)—C(14)—F(5)	107.7(2)
C(6)—C(5)—C(4)	108.5(2)	F(4)—C(14)—F(5)	107.7(3)
C(5)—C(6)—C(7)	104.1(2)	F(6)—C(14)—C(3)	111.3(2)
C(6)—C(7)—C(8)	109.4(2)	F(4)—C(14)—C(3)	111.2(2)
C(6)—C(7)—C(11)	104.0(2)	F(5)—C(14)—C(3)	110.6(2)
C(8)—C(7)—C(11)	106.8(2)	F(8)—C(17)—F(7)	108.5(2)
O(16)—C(8)—O(12)	106.2(2)	F(8)—C(17)—F(9)	107.5(3)
O(16)—C(8)—C(9)	115.2(2)	F(7)—C(17)—F(9)	107.2(3)
O(12)—C(8)—C(9)	106.5(2)	F(8)—C(17)—C(11)	111.6(3)
O(16)—C(8)—C(7)	108.6(2)	F(7)—C(17)—C(11)	110.6(2)
O(12)—C(8)—C(7)	108.1(2)	F(9)—C(17)—C(11)	111.3(2)

least-squares in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were located objectively from the difference Fourier map and refined isotropically. The final discrepancy factors are $R_1 = 0.065$ (1913 independent reflections with $I > 2\sigma(I)$) and $wR_2 = 0.169$ (2292 independent reflections). All calculations were carried out on IBM-PC/AT-486 using the SHELXTL PLUS programs.[10]

6-Hydroxy-9-oxo-2,4,10-tris(trifluoromethyl)-3,11,12-trioxatetracyclo[5.2.1.0^{2,6}.0^{4,10}]dodecane (2). *From acetonylacetone.* Lithium hydride (0.4 g, 0.05 mol) was added to a solution of CF_3CO_2Me (12.8 g, 0.1 mol) in 50 mL of anhydrous THF, followed by addition of acetonylacetone (1.14 g, 0.01 mol) with stirring at 20 °C for 1 h. The reaction mixture was stirred at room temperature for 2 h, refluxed for additional 6 h, concentrated to one third of the initial volume, and poured into 100 mL of cold 10% H_2SO_4. The organic material was extracted with ether (4×30 mL). The extracts were combined and dried over $MgSO_4$. The ether was removed, and the residue evacuated. A resinous product crystallized over a week was washed with hot chloroform, dissolved in acetone, and precipitated with benzene. Yield 0.96 g (24%), m.p. 197—198 °C. Found (%): C, 35.97; H, 1.68; F, 42.68. $C_{12}H_7F_9O_5$. Calculated (%): C, 35.84; H, 1.75; F, 42.52. ^{19}F NMR (acetone-d_6), δ: 77.94, 82.24, 85.68 (all s, each 3 F, 3 CF_3). IR (paste, Vaseline oil), ν/cm^{-1}: 3290 (O—H), 1475 (C=O).

From bis(β-diketone) **1**. Anhydrous THF (50 mL), lithium hydride (0.28 g, 0.035 mol), and tetraketone **1** (3.06 g, 0.01 mol) were placed in a 100-mL flask.[7] The reaction mixture was refluxed until hydrogen evolution ceased. CF_3CO_2Me (10.2 g, 0.08 mol) was added, and refluxing was continued for 6 h. Subsequent workup was carried out as described above. The yield of compound **2** was 2.1 g (52%).

This work was financially supported by the Russian Foundation for Basic Research (Projects Nos. 00-03-32840a and 00-15-97359).

References

1. V. V. Korshak, E. S. Krongauz, A. M. Sladkov, V. E. Sheina, and L. K. Luneva, *Vysokomol. Soedin.*, 1959, **1**, 1764 [*Polym. Sci. USSR*, 1959, **1** (Engl. Transl.)].
2. P. van der Valk and P. G. Potvin, *J. Org. Chem.*, 1994, **59**, 1766; V. I. Saloutin, K. I. Pashkevich, and I. Ya. Postovskii, *Zh. Vses. Khim. O-va im. D. I. Mendeleeva*, 1981, **26**, 105 [*Mendeleev Chem. J.*, 1981, **26** (Engl. Transl.)].
3. V. V. Korshak, E. S. Krongauz, A. M. Berlin, and P. N. Gribkova, *Dokl. Akad. Nauk SSSR*, 1963, **149**, 602 [*Dokl. Chem.*, 1963 (Engl. Transl.)].
4. F. Martin, M. Shamma, and W. K. Fernelius, *J. Am. Chem. Soc.*, 1958, **40**, 4891.
5. K. G. Hampton and J. J. Christie, *J. Org. Chem.*, 1975, **40**, 3887; K. G. Hampton and J. J. Christie, *J. Org. Chem.*, 1976, **41**, 2772.
6. K. I. Pashkevich, V. I. Saloutin, and I. Ya. Postovskii, *Dokl. Akad. Nauk SSSR*, 1977, **234**, 600 [*Dokl. Chem.*, 1977 (Engl. Transl.)].
7. D. L. Chizhov, V. G. Ratner, M. I. Kodess, and K. I. Pashkevich, *Zh. Org. Khim.*, 1998, **34**, 371 [*Russ. J. Org. Chem.*, 1998, **34** (Engl. Transl.)].
8. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
9. M. L. Miles, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, 1965, **30**, 1007.
10. G. M. Sheldrick, *SHELXTL PC. Version 5.0. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data. Siemens Analytical X-Ray Instruments*, Inc., Madison, WI, 1994.

Received August 18, 1999;
in revised form August 18, 2000