Letters to the Editor

Synthesis and tautomeric equilibrium of 2,6-bis(trifluoroacetyl)cyclohexanone

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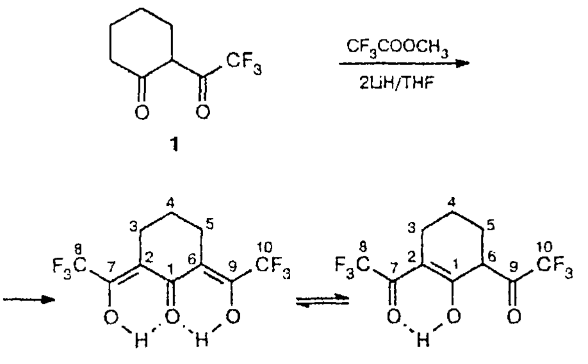
Condensation of 2-trifluoroacetylcyclohexanone[1] (1) with methyl trifluoroacetate in the presence of a double excess of lithium hydride allowed us to obtain for the first time 2,6-bis(trifluoroacetyl)cyclohexanone (2).



2

Compound 2, the first representative of 2,4-(*n*-methylene)substituted polyfluoroalkyl-containing 1,3,5-triketones, is of interest not only as a starting compound for the synthesis of new heterocyclic systems but also as a parent compound for studying the features of keto-enol tautomerism of fluorinated 1,3,5-tricarbonyl compounds, which, in this case, is not complicated by a ring-chain 1,3,5-triketone→4-pyrone transformation, characteristic of 1,3,5-triketones.[2]

^1H, ^{19}F, and ^{13}C NMR spectroscopy study showed that compound 2 exists in $CDCl_3$ in two tautomeric forms (in the ratio 80 : 20). The main tautomer **A** has the symmetrical dienediol structure with the *Z*-configuration of the exocyclic double bonds. This is confirmed by the presence of a two-proton quartet in the ^1H NMR spectrum at δ 14.67, which is well-resolved owing to far spin-spin coupling with the fluorine atoms of the trifluoromethyl group ($^4J_{H-F}$ = 2.0 Hz), and by the ^{13}C chemical shifts of the C(1), C(2,6), and C(7,9) atoms (the assignment of the latter is unambiguous because of spin-spin coupling with the fluorine atoms). The *Z*-configuration of the enol double bonds of the main tautomer is also evidenced by far spin-spin coupling with both the enol proton and the ring CH_2 protons ($^5J_{H-F}$ = 1.8 Hz) in the ^{19}F NMR spectrum (recorded at a digital resolution of 0.122 Hz per point). This spin-spin coupling disappears when the corresponding protons are suppressed in the double resonance $^{19}F\{^1H\}$ NMR spectrum.

The ^{19}F NMR spectrum of the minor tautomer contains signals for the two nonequivalent CF_3 groups, and the ^1H NMR spectrum contains signals for the methyne and enol protons, which suggests a nonsym-

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metrical monoenol structure. Among three nonsymmetrical tautomers that are possible for compound **2**, structure **B** with the endocyclic double bond was chosen with consideration of ^{13}C NMR spectroscopy data: the signals for C(7) and C(9) are shifted downfield (as compared to tautomer **A**), which confirms that they belong to the carbonyl groups, and the signal for C(1) is shifted upfield, thus suggesting that this atom is involved in enolization. The ^{13}C NMR spectral data of tautomers **A** and **B** are in accord with the regularity noted earlier,[3] *viz.*, the direct spin-spin coupling constant $^1J_{C-F}$ in the trifluoromethyl group markedly increases on going from the $CF_3-C=C$ to $CF_3-C=O$ fragment, though this regularity is not of general character.[4]

2,6-Bis(trifluoroacetyl)cyclohexanone (2). A solution of 1,3-diketone **1** (5.0 g, 26 mmol) and methyl trifluoroacetate (7.7 g, 60 mmol) in 25 mL of anhydrous THF was added dropwise for 30 min with vigorous stirring to a suspension of LiH (0.42 g, 52 mmol) in 50 mL of anhydrous THF and refluxed for 12 h. Two thirds of the solvent was distilled off, and the residue was treated with 100 mL of 10% H_2SO_4. The product was extracted with $CHCl_3$, and the extract was dried with $MgSO_4$. Compound **2** was isolated by vacuum distillation. Yield 4.0 g (53%), colorless crystals, m.p. 36—37 °C, b.p. 108—110 °C (15 Torr). Found (%): C, 41.22; H, 2.86; F, 39.18. $C_{10}H_8F_6O_3$. Calculated (%): C, 41.39; H, 2.78; F, 39.28. IR (Vaseline oil), ν/cm^{-1}: 1580, 1630 (C=O). NMR spectra were recorded in $CDCl_3$ with Me_4Si (^{1}H and ^{13}C) and C_6F_6 (^{19}F) as the internal standards. Tautomer **A**. ^{1}H NMR, δ: 1.77 (m, 2 H, CH_2); 2.57 (m, 4 H, 2 CH_2); 14.67 (q, 2 H, 2 OH, $^4J_{H-F}$ = 2.0 Hz). ^{19}F NMR, δ: 93.36 (dt, 6 F, 2 CF_3, $^4J_{F-OH}$ = 2.0 Hz, $^5J_{F-CH}$ = 1.8 Hz). ^{13}C NMR, δ: 21.53 (s, C(4)); 22.89 (q, C(3,5), $^4J_{C-F}$ = 2.4 Hz); 108.59 (q, C(2,6), $^3J_{C-F}$ = 1.8 Hz); 119.20 (q, C(8,10), $^1J_{C-F}$ = 278.9 Hz); 160.74 (q, C(7,9), $^2J_{C-F}$ = 35.4 Hz); 195.98 (s, C(1)).

Tautomer **B**. ^{1}H NMR, δ: 1.77 (m, 2 H, CH_2); 2.57 (m, 4 H, 2 CH_2); 4.06 (t, 1 H, CH, $^3J_{H-H}$ = 6.7 Hz); 14.40 (s, 1 H, OH). ^{19}F NMR, δ: 84.18 (s, 3 F, C(10)F_3); 88.39 (t, 3 F, C(8)F_3, $^5J_{F-CH}$ = 1.2 Hz). ^{13}C NMR, δ: 19.74, 21.22, 24.56 (C(3), C(4), C(5)); 48.88 (s, C(6)); 106.54 (s, C(2)); 115.37 (q, C(10), $^1J_{C-F}$ = 291.8 Hz); 116.94 (q, C(8), $^1J_{C-F}$ = 286.9 Hz); 180.09 (s, C(1)); 180.97 (q, C(7), $^2J_{C-F}$ = 35.4 Hz); 189.08 (q, C(9), $^2J_{C-F}$ = 36.6 Hz).

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