Letters to the Editor

Ring-chain isomerism in a series of α-hydroxyoxoenamines. Isomeric transformations of the product of condensation of 1-acetylcyclohexanol with trifluoroacetonitrile

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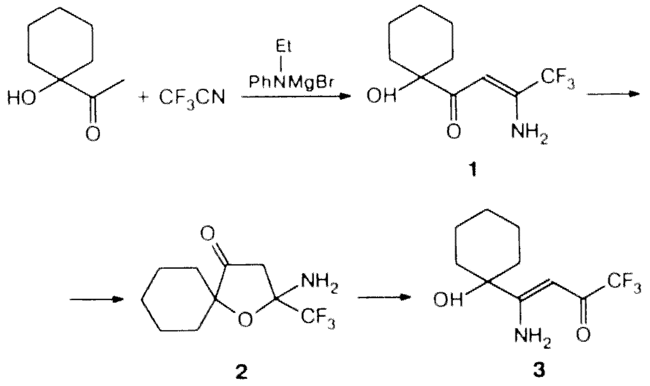
We have shown that the condensation of 1-acetylcyclohexanol with trifluoroacetonitrile in the presence of ethylphenylaminomagnesium bromide results in the formation of α-hydroxyoxoenamine (**1**) isolated from its copper chelate by hydrogen sulfide in a 36 % yield. After 4 months of storage at room temperature, α-hydroxyoxoenamine **1** cyclized spontaneously to aminotetrahydrofuranone **2**, which then isomerized to hydroxyaminoenone (**3**) after 2.5 years with 60 % conversion. Attempts to accelerate the opening of the tetrahydrofuran cycle of compound **2** to form isomer **3** by heating in a sealed tube resulted in the formation of a complex mixture of products of the self-condensation of 1-acetylcyclohexanol.



The transformation of aminotetrahydrofuran **2** to the acyclic form **3** has no analogs in the literature, although the isomerization of aminovinyl ketones with the geminal arrangement of the amino group and a perfluoroalkyl substituent to form aminovinyl ketones with the γ-arrangement of these groups has been described.[1,2] The driving force of process **1** → **2** → **3** is evidently the fact that the thermodynamic stability of hydroxyoxoenamine **3** is greater than that of hydroxyoxoenamine **1** due to the stronger intramolecular hydrogen bond in the aminoenone fragment of compound **3**, which is evidenced by two signals of nonequivalent amino group protons in the ^{1}H NMR spectrum.

5-Amino-1,1,1-trifluoro-5-hydroxy-5,5-pentamethylenepent-2-en-4-one (1). Yield 36 %, m.p. 69—70 °C (from pentane). Found (%): C, 50.60; H, 5.84; N 5.80. $C_{10}H_{14}F_3NO_2$. Calculated (%): C, 50.63; H, 5.95; N, 5.90. IR (Vaseline oil), ν/cm^{-1}: 3440, 3380, 3280, 3180 (OH, NH_2); 1640, 1605, 1550 (NH_2, C=C—C=O). ^{1}H NMR ($CDCl_3$), δ: 1.62 (m, 10 H, $(CH_2)_5$); 3.78 (s, 1 H, OH); 5.75 (s, 1 H, =C—H); 7.3 (br.s, 2 H, NH_2).

5-Amino-5-trifluoromethyl-2,2-pentamethylenetetrahydrofuran-3-one (2). M.p. 79—80 °C (from hexane). Found (%): C, 50.74; H, 6.01; N 5.83. $C_{10}H_{14}F_3NO_2$. Calculated (%): C, 50.63; H, 5.95; N, 5.90. IR (Vaseline oil), ν/cm^{-1}: 3420, 3350 (NH_2); 1740 (C=O); 1640 (NH_2). ^{1}H NMR ($CDCl_3$), δ: 1.62

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(m, 10 H, $(CH_2)_5$); 2.08 (s, 2 H, NH_2); 2.52, 2.98 (d.d, 2 H, H_A, H_B, J = 18.5 Hz).

4-Amino-1,1,1-trifluoro-5-hydroxy-5,5-pentamethylene-pent-3-en-2-one (3). M.p. 127—128 °C. Found (%): C, 50.70; H, 5.91; N 5.92. $C_{10}H_{14}F_3NO_2$. Calculated (%): C, 50.63; H, 5.95; N, 5.90. IR (Vaseline oil), ν/cm^{-1}: 3410, 3310, 3210 (OH, NH_2); 1605, 1530 (NH_2, C=C—C=O). ^{1}H NMR ($CDCl_3$), δ: 1.69 (m, 10 H, $(CH_2)_5$); 2.14 (s, 1 H, OH); 5.39 (d, 1 H, =CH, J = 1.6 Hz); 7.4, 10.4 (br.s, 2 H, NH_2).

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Reactions of fullerenes with deuterium in the presence of palladium

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It has been reported[1] that fullerene deuteride $C_{60}D_x$ has been obtained as the result of the reaction between gaseous deuterium and palladium fulleride under rather mild conditions (473 K, 2 MPa). Mass spectrometric analysis of the obtained deuteride $C_{60}D_x$ showed that x varies from 2 to >30 with local maxima at 2, 4, 18, and 26. It was also mentioned that palladium clusterization took place during the reaction. These observations gave reason to believe that palladium clusters take an active part in the gas phase deuteration of fullerenes.

In this work, we report the results of an investigation of the reaction of D_2 with fullerite (78 % C_{60} + 22 % C_{70}) in the presence of palladium clusters (Pd/C catalyst, specific surface of the carrier ~350 m^2/g, Pd content 10 wt. %) as well as of palladium metallic powder (average size of the particles was ~10 mm.)

A homogeneous mixture of Pd or Pd/C (50 wt. %) + Ful (50 wt. %), where Ful is fullerite, was obtained by stirring in a vibration mill (amplitude 10 mm, ball load 50 : 1, argon medium, time 30 min.). Degasification of the mixture was carried out before deuteration by heating up to 500 K *in vacuo* (~1 Pa). Deuterium was injected after the sample had cooled down to 300 K. Deuteriation was carried out at pressures from 1.0 to 2.5 MPa and temperatures from 473 K to 673 K. The reaction products were removed from an autoclave in an inert atmosphere after they had cooled to room temperature.

An *endo*-effect followed by liberation of ~1 wt. % of gas, which corresponds to deuterium liberation from palladium deuteride of the composition of $PdD_{0.9}$, can be seen on the thermogravigram of deuterated mixtures of Pd + Ful at 373 to 400 K in an argon atmosphere. A second *endo*-effect with gas liberation can be clearly seen at ~800 K. Depending on the conditions of the deuteriation of the initial mixture, the weight loss was from 0 (473 K, 1 MPa, 1 h) to 3.5 wt. % (673 K, 2.5 MPa, 10 cycles of "heating to 673 K (1 h) ⇔ cooling to 293 K (1 h)"). Apparently, the second *endo*-effect was due to the decomposition of fullerene deuteride with liberation of gaseous deuterium, which is consistent with the available published data for the decomposition of fullerene hydride.[2,3] The second *endo*-effect is also clearly seen in the samples of the Pd/C + Ful deuterated mixture. The small value of the first *endo*-effect (weight loss at ~385 K) for these samples is connected with the small amount of Pd in them.

There is an absorption band in the IR spectra of the deuterated samples with a maximum at 2120 cm^{-1},

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