performed in a full-matrix anisotropic approximation. The isotropic thermal parameters of hydrogen atoms were not refined, but fixed equal to values that are a factor of 1.5 greater than the corresponding parameters of non-hydrogen atoms. The final R value obtained from 1604 reflections with $I > 2\sigma(I)$ is equal to 0.050. All computations were performed on a PC/AT using the SHELX-86 [3] and SHELXL-193 [4] programs. The coordinates of atoms are listed in Table 4.

The quantum-chemical calculations for the A and B forms of compound 2a were performed by the MNDO [2] method on a PC/AT.

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A simple synthesis of 4-amino-6-methyl-1,1,1-trifluoro(trichloro)hepta-3,5-dien-2-ones and 2,2-dimethyl-6-trifluoromethyl-2,3-dihydro-4-pyridone

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Treatment of 2,2-dimethyl-6-trifluoro(trichloro)methyl-2,3-dihydro-4-pyrones with ammonia gives 4-amino-1,1,1-trifluoro(trichloro)-6-methylhepta-3,5-dien-2-ones. Under similar conditions 1,1,1-trifluoro-2-hydroxy-6-methylhepta-2,5-dien-4-one and 6-chloro-1,1,1-trifluoro-2-hydroxy-6-methylhept-2-en-4-one cyclize into 2,2-dimethyl-6-trifluoromethyl-2,3-dihydro-4-pyridone.

Key words: aminodienones, β-diketones, dihydropyrones, ammonia, heterocyclization; 2,3-dihydro-2,2-dimethyl-6-trifluoromethyl-4-pyridone.

Earlier,[1] we demonstrated that the condensation of trifluoroacetonitrile with mesityl oxide in the presence of *N*-ethylanilinemagnesium bromide leads to 2-amino-1,1,1-trifluoro-6-methylhepta-2,5-dien-4-one (**1**), whose acid hydrolysis can give, depending on reaction conditions, either 1,1,1-trifluoro-2-hydroxy-6-methylhepta-2,5-dien-4-one (**2**) or its cyclic isomer, 2,2-dimethyl-6-trifluoromethyl-2,3-dihydro-4-pyrone (**3**). The cyclization of dienone **2** into dihydropyrone **3** is catalyzed by acids, while the reverse process occurs under the action of sodium ethoxide.

In continuation of studies on the properties of these compounds, we found that dihydropyrone **3** treated with an aqueous 25% solution of ammonia at room temperature undergoes ring opening to give 4-amino-1,1,1-trifluoro-6-methylhepta-3,5-dien-2-one (**4**) isomeric to aminodienone **1**, while dienone **2**, under similar conditions, undergoes heterocylization into 2,2-dimethyl-6-trifluoromethyl-2,3-dihydro-4-pyridone (**5**). The yields of products **4** and **5** are 46 and 37%, respectively, and a competitive reaction is the cleavage of compounds **2** and **3** under the action of ammonia into mesityl oxide and CF_3COONH_4. The treatment of 6-chloro-1,1,1-trifluoro-2-hydroxy-6-methylhept-2-en-4-one (**6**), obtained upon acidic hydrolysis of chloroaminoenone (**7**) described earlier,[1] with aqueous ammonia can also result in dihydropyridone **5** (Scheme 1).

In the preparative synthesis of compounds **4** and **5**, the more readily available ethyl trifluoroacetate rather than trifluoroacetonitrile is recommended. Its condensation with mesityl oxide in the presence of sodium methoxide followed by the isolation of the product through a copper chelate gives dienone **2** in a high yield.[2] The same reaction can also be used to obtain dihydropyrone **3**, if the condensation product is isolated by vacuum distillation, without the stage of formation of a copper chelate.

2,2-Dimethyl-6-trichloromethyl-2,3-dihydro-4-pyrone (**8**) behaves similarly to dihydropyrone **3**.[3] Its

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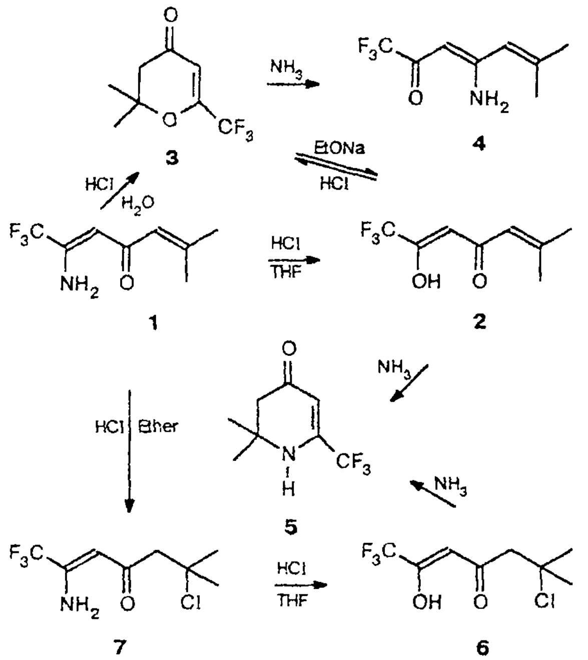
Scheme 1



treatment with a methanolic ammonia leads to 4-amino-1,1,1-trichloro-6-methylhepta-3,5-dien-2-one (**9**) in 32% yield.

The reactions described above are simple and make compounds **4**—**6** and **9**, which are of interest as new CF_3- and CCl_3-containing synthons, more readily available.

Experimental

IR spectra were recorded on an IKS-29 instrument in Vaseline oil or in a thin layer. ^1H NMR spectra were recorded on a Tesla BS-567A spectrometer (100 MHz) in $CDCl_3$ with tetramethylsilane as the internal standard.

Compounds **1**, **2**, and **7** (see Ref. 1) and **3** and **8** (see Ref. 3) were described previously.

4-Amino-6-methyl-1,1,1-trifluorohepta-3,5-dien-2-one (4). 4 mL of an aqueous 25% solution of NH_3 was added to dihydropyrone **3** (0.39 g, 0.002 mol) and the mixture was left to stand at ~20 °C for 2 days. The crystals that formed were filtered off and recrystallized from a hexane—ether mixture, yield 46%, m.p. 72—73°C. Found (%): C, 49.55; H, 5.24; N, 6.96. $C_8H_{10}F_3NO$. Calculated (%): C, 49.74; H, 5.22; N, 7.25. IR, ν/cm^{-1}: 3310, 3160 (NH_2); 1650, 1600, 1540 (C=C—C=O, NH_2). ^1H NMR, δ: 1.91 (d, 3 H, Me, J = 1.4 Hz); 1.98 (d, 3 H, Me, J = 1.2 Hz); 5.38 (d, 1 H, =CH, J = 1.4 Hz); 5.76 (sept, 1 H, =CH, J = 1.2 Hz); 5.80 (br.s, 1 H, NH_2); 10.10 (br.s, 1 H, NH_2).

2,2-Dimethyl-6-trifluoromethyl-2,3-dihydro-4-pyridone (5) was obtained from diketone **2** analogously to compound **4**. Yield 37%, m.p. 114—115 °C. Found (%): C, 49.56; H, 5.14; N, 7.51. $C_8H_{10}F_3NO$. Calculated (%): C, 49.74; H, 5.22; N, 7.25. IR, ν/cm^{-1}: 3260 (NH); 1645, 1600, 1540 (C=C—C=O, NH). ^1H NMR, δ: 1.37 (s, 6 H, 2 Me); 2.44 (s, 2 H, CH_2); 4.94 (br.s, 1 H, NH); 5.38 (d, 1 H, =CH, J = 1.9 Hz).

2-Hydroxy-6-methyl-6-chloro-1,1,1-trifluorohept-2-en-4-one (6) was obtained according to a procedure described earlier.[1] Yield 65%, b.p. 60—63 °C (10 Torr), n_D^{20} 1.4400. Found (%): C, 41.84; H, 4.49. $C_8H_{10}ClF_3O_2$. Calculated (%): C, 41.67; H, 4.37. IR, ν/cm^{-1}: 1640 (C=O); 1600 (C=C). ^1H NMR, δ: 1.71 (s, 6 H, 2 Me); 2.87 (s, 2 H, CH_2); 6.04 (s, 1 H, =CH); 13.70 (br.s, 1 H, OH).

4-Amino-6-methyl-1,1,1-trichlorohepta-3,5-dien-2-one (9). 3 mL of a methanolic NH_3 was added to dihydropyrone **8** (0.5 g, 0.002 mol) and the mixture was left to stand at ~20 °C for 2 days. Then, the solution was diluted with water, extracted with ether, and dried with Na_2SO_4. The crystals obtained upon evaporation of the ether were recrystallized from hexane. Yield 32%, m.p. 94—95 °C. Found (%): C, 39.74; H, 4.07; N, 5.71. $C_8H_{10}Cl_3NO$. Calculated (%): C, 39.62; H, 4.16; N, 5.78. IR, ν/cm^{-1}: 3330, 3170 (NH_2); 1655, 1585, 1515 (C=C—C=O, NH_2). ^1H NMR, δ: 1.92 (d, 3 H, Me, J = 1.4 Hz); 2.00 (d, 3 H, Me, J = 1.4 Hz); 5.73 (d, 1 H, =CH, J = 1.2 Hz); 5.81 (sept, 1 H, =CH, J = 1.4 Hz); 5.60 (br.s, 1 H, NH_2); 9.6 (br.s, 1 H, NH_2).

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