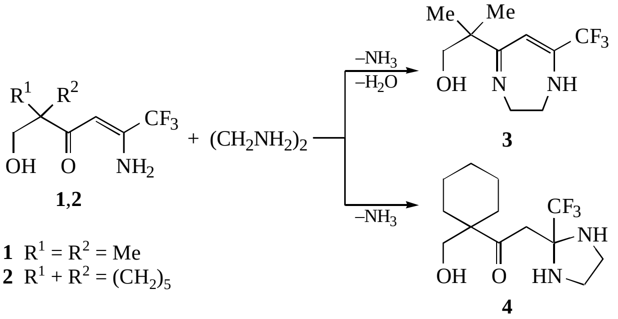
Unexpected synthesis of 2-(3-hydroxymethyl-3,3-pentamethyleneacetonyl)-2-trifluoromethylimidazolidine

Vyacheslav Ya. Sosnovskikh* and Michail Yu. Mel'nikov

Department of Chemistry, A. M. Gor'ky Urals State University, 620083 Ekaterinburg, Russian Federation. Fax: +7 3432 615 978; e-mail: Vyacheslav.Sosnovskikh@usu.ru

The reaction of 2-amino-6-hydroxy-5,5-pentamethylene-1,1,1-trifluoro-2-hexen-4-one with ethylenediamine, in contrast to the similar reaction involving 2-amino-6-hydroxy-5,5-dimethyl-1,1,1-trifluoro-2-hexen-4-one, leads to 2-(3-hydroxymethyl-3,3-pentamethyleneacetonyl)-2-trifluoromethylimidazolidine.



It is known[1] that ethylenediamine reacts with β-amino-β-polyfluoroalkylvinylketones at two electrophilic centres simultaneously to produce 2,3-dihydro-1,4-diazepines. In an attempt to synthesize diazepines containing such substituents as the trifluoromethyl and hydroxyalkyl groups, we found that 2-amino-6-hydroxy-5,5-dimethyl(pentamethylene)-1,1,1-trifluoro-2-hexen-4-ones **1**,**2**, obtained by the condensation of 4-hydroxy-3,3-dimethyl(pentamethylene)butan-2-ones with trifluoroacetonitrile,[2] react with ethylenediamine in quite different ways although their structures are very similar. For instance, aminoenone **1** gives the expected diazepine **3** in a 75% yield, while aminoenone **2** gives imidazolidine **4** in the same yield under these conditions.[†]

In the latter case, double nucleophilic attack at the β-carbon atom with elimination of an ammonia molecule takes place, while the carbonyl group is retained, most likely due to steric factors.

The formation of 2-trifluoromethyl-2-ethoxycarbonylmethylimidazolidine from the reaction of ethylenediamine with ethyl trifluoroacetoacetate has been reported previously,[3] but the literature contains no data regarding this reaction pathway involving β-amino-β-polyfluoroalkylvinylketones. At present, we are trying to clarify whether the formation of imidazolidine **4** revealed here is a characteristic property of β-amino-β-polyfluoroalkylvinylketones or if this reaction presents a specific case caused by the structural features of aminoenone **2**.

This work was supported by the Russian Foundation for Basic Research (grant no. 96-03-33373).

References

1 K. I. Pashkevich, A. Ya. Aizikovich and I. Ya. Postovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 455 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 420).
2 V. Ya. Sosnovskikh and M. Yu. Mel'nikov, *Zh. Org. Khim.*, 1998, in press.
3 G. M. J. Slusarczuk and M. M. Joullie, *J. Org. Chem.*, 1971, **36**, 37.

Received: Moscow, 3rd October 1997
Cambridge, 28th November 1997; Com. 7/07584G

[†] 2,3-*Dihydro*-5-*trifluoromethyl*-7-(2-*hydroxy*-1,1-*dimethylethyl*)-1,4-*diazepine* **3**. Aminoenone **1** (300 mg, 1.4 mmol) was dissolved in 400 μl (360 mg, 6.0 mmol) of ethylenediamine, and the reaction mixture was kept for three days at room temperature. The resulting crystals of diazepine **3** were recrystallised from hexane, yield 250 mg (75%), mp 130–131 °C. Found (%): C 50.87, H 6.53, N 11.73. Calc. for $C_{10}H_{15}F_3N_2O$ (%): C 50.84; H 6.40; N 11.86. IR (vaseline oil, ν/cm^{-1}): 3345, 3140 (NH, OH), 1620, 1570, 1550 (C=N, C=C, NH). ^{1}H NMR (80 MHz, $CDCl_3$) δ: 1.19 (s, 6H, $2CH_3$), 2.9 (br. s, 2H, OH, NH), 3.50 (br. s, 2H, CH_2N), 3.57 (s, 2H, CH_2O), 3.78 (t, 2H, $CH_2N=$), 5.07 (s, 1H, =CH).

2-(3-*Hydroxymethyl*-3,3-*pentamethyleneacetonyl*)-2-*trifluoromethylimidazolidine* **4** was obtained from 200 mg of aminoenone **2** under the same conditions as diazepine **3**. Yield 180 mg (76%), mp 85–86 °C (hexane). Found (%): C 53.26; H 7.32; N 9.59. Calc. for $C_{13}H_{21}F_3N_2O_2$ (%): C 53.05; H 7.19; N 9.52. IR (vaseline oil, ν/cm^{-1}): 3360 , 3315, 3195 (NH, OH), 1705 (C=O), 1645 (NH). ^{1}H NMR (80 MHz, $CDCl_3$) δ: 1.2–2.0 [m, 10H, $(CH_2)_5$], 2.90 (s, 2H, CH_2), 3.02 (s, 4H, CH_2CH_2), 3.4 (br. s, 3H, OH, 2NH), 3.72 (s, 2H, CH_2O).