Brief Communications

Unexpected synthesis of 6-amino-2,3-dihydro-4-pyrone-3-spirocyclohexane

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The reaction of 2-amino-2-(trichloromethyl)tetrahydro-4-pyrone-5-spirocyclohexane with ethylenediamine afforded 6-amino-2,3-dihydro-4-pyrone-3-spirocyclohexane, whereas 2-amino-5,5-dimethyl-2-(trichloromethyl)tetrahydro-4-pyrone gave 2-(3-hydroxy-2,2-dimethylpropionylmethylene)imidazolidine in low yield.

Key words: 5,5-dialkyl-2-amino-2-(trichloromethyl)tetrahydro-4-pyrones, ethylenediamine, 6-amino-2,3-dihydro-4-pyrone-3-spirocyclohexane, 2-(3-hydroxy-2,2-dimethylpropionylmethylene)imidazolidine.

Previously,[1] we have demonstrated that condensation of 3,3-dialkyl-4-hydroxy-2-butanones with trichloroacetonitrile in the presence of *N*-ethylanilinomagnesium bromide did not afford the expected β-amino-β-(trichloromethyl)vinyl ketones; instead, their cyclic isomers, *viz.*, 5,5-dialkyl-2-amino-2-(trichloromethyl)tetrahydro-4-pyrones **1a**,**b**, were obtained.

Earlier, we have prepared[2,3] 2-acylmethyleneimidazolidines by the reactions of β-amino-β-(trichloromethyl)vinyl ketones with ethylenediamine (EDA). Hence, compounds **1a**,**b** would be expected to behave analogously. However, in spite of the structural similarity of compounds **1a** and **1b**, their reactions with EDA at ~20 °C in the absence of a solvent proceeded differently. Thus, the reaction of tetrahydropyrone **1a** with EDA was accompanied by the ring opening and the replacement of the CCl_3 and NH_2 groups to give the expected imidazolidine **2**, whereas the analogous reaction with compound **1b** proceeded with retention of the ring and elimination of the chloroform molecule to form dihydropyrone **3** in 72% yield (Scheme 1).

Apparently, the reaction began with the replacement of the CCl_3 group and proceeded through common intermediate **4**, which was subsequently decomposed either with elimination of the ammonia molecule followed by recyclization of intermediate **5** to form imidazolidine **2** or with elimination of the EDA molecule to yield dihydropyrone **3**. The closest analogs of compound **3** described in the literature[4,5] are 2,2-dialkyl-5-amino-2,3-dihydrofuran-3-ones.

In the ^{1}H NMR spectrum of compound **3** in $CDCl_3$, which was recorded after the addition of CD_3CO_2D, the singlet of the CH_2O group at δ 4.24 persisted, whereas signals of both the NH_2 group and the vinyl proton disappeared, which is indicative of the tautomeric equilibrium between the ketoenamine and ketoimine forms. It should

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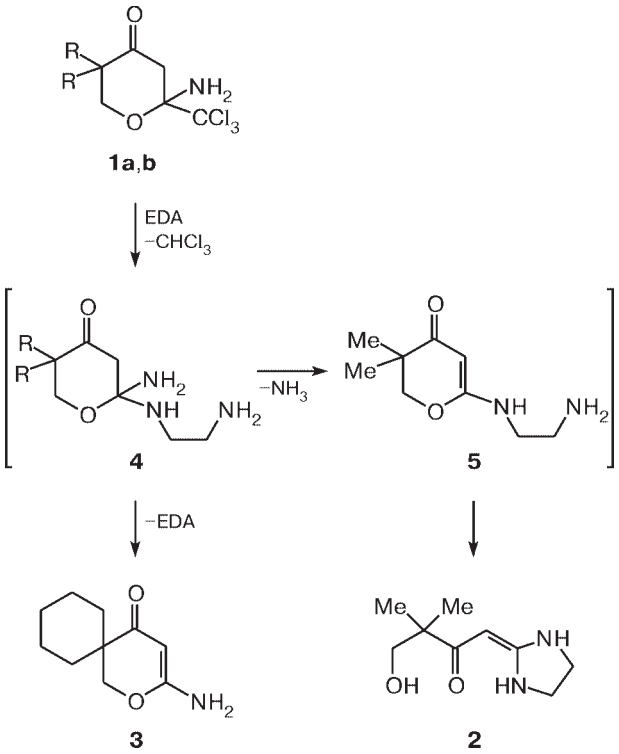
Scheme 1



a: R = Me; **b:** R + R = $(CH_2)_5$

also be noted that the ^{1}H NMR spectrum, which was measured after the addition of CD_3CO_2D to a chloroform solution of imidazolidine **2**, has two sets of signals. One of these sets belongs to the expected imidazolinium cation (80%) and the second set corresponds to deuterated dihydropyrone **5** (20%), which is the most probable intermediate in the reaction giving rise to imidazoline **2** from compound **1a**. Previously,[3] an analogous situation has been observed for 2-methyleneimidazolidines containing the α-ketol fragments.

Experimental

The IR spectra were measured on an IKS-29 instrument in Nujol mulls. The ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer (250.13 MHz) in $CDCl_3$ with Me_4Si as the internal standard.

6-Amino-2,3-dihydro-4-pyrone-3-spirocyclohexane (3). Tetrahydropyrone **1b** (0.3 g, 1.0 mmol) was dissolved in ethylenediamine (0.3 mL, 0.27 g, 4.5 mmol). The reaction mixture was kept at ~20 °C for 3 days. The crystals of dihydropyrone **3** that formed were washed with water and recrystallized from CCl_4, the yield was 0.13 g (72%), m.p. 196—197 °C. Found (%): C, 66.33; H, 8.39; N, 7.73. $C_{10}H_{15}NO_2$. Calculated (%): C, 66.27; H, 8.34; N, 7.73. IR, ν/cm^{-1}: 3350, 3185 (NH_2); 1660 (C=O); 1550, 1510 (C=C, NH_2). ^{1}H NMR, δ: 1.26—1.83 (m, 10 H, $(CH_2)_5$); 4.24 (s, 2 H, CH_2O); 4.65 (s, 1 H, CH=); 4.68 (br.s, 2 H, NH_2); after the addition of CD_3CO_2D: 1.25—1.83 (m, 10 H, $(CH_2)_5$); 4.25 (s, 2 H, CH_2O).

2-(3-Hydroxy-2,2-dimethylpropionylmethylene)imidazolidine (2) was prepared analogously to compound **3**, the yield was 15%, m.p. 142—143 °C. Found (%): C, 58.37; H, 8.68; N, 15.50. $C_9H_{16}N_2O_2$. Calculated (%): C, 58.67; H, 8.75; N, 15.21. IR, ν/cm^{-1}: 3380, 3270, 3220 (OH, NH); 1615 (C=O); 1560 (br, C=C, NH). ^{1}H NMR, δ: 1.13 (s, 6 H, 2 Me); 3.50 (s, 2 H, CH_2O); 3.56 (m, 2 H, CH_2); 3.70 (m, 2 H, CH_2); 4.30 (br.s, 1 H, OH); 4.83 (s, 1 H, =CH); 4.87 (br.s, 1 H, NH); 9.28 (br.s, 1 H, NH); after the addition of CD_3CO_2D, cation **2** (80%): 1.11 (s, 6 H, 2 Me); 3.59 (s, 2 H, CH_2O); 3.86 (s, 4 H, CH_2CH_2); cation **5** (20%): 1.07 (s, 6 H, 2 Me); 3.16 (br.s, 2 H, CH_2); 3.50 (br.s, 2 H, CH_2); 4.05 (s, 2 H, CH_2O).

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