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SHORT COMMUNICATIONS

Selective Reduction of C=C Bond in Iminolactone Ring by a System Magnesium–Methanol

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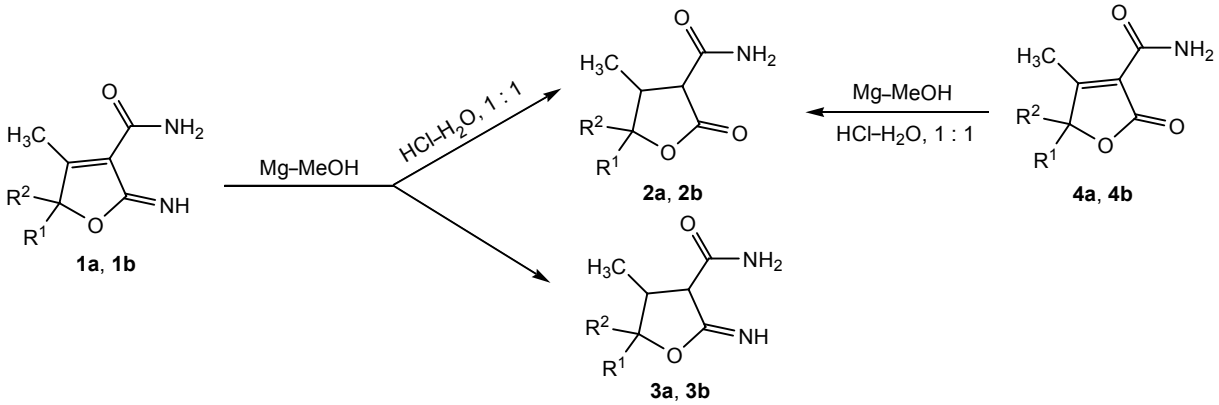
We formerly developed a convenient method of preparation of unsatrurated γ-iminolactones by reaction in the presence of sodium methylate of tertiary α-ketoalcohols and amides (nitriles) of acids containing an active methylene group [1–6]. We attempted to perform a transition from the unsaturated to saturated γ-iminolactones by selective reduction of the C=C bond in the iminolactone ring not affecting the functional groups.

The reduction with molecular hydrogen is sometimes impossible, firstly, because of the hazards met when working with it, and secondly, due to the inaccessibility of reduction catalysts [7]. The use of complex metal hydrides ($LiAlH_4$, $NaBH_4$) results in the cleavage of the ring and glycol formation [8, 9]. A system magnesium–methanol is used for reductive cyclization, reductive cleavage, for reduction of certain substituents (NO_2, N_3, Cl, oxime group) and of conjugated C=C bond [10–12].

The system magnesium–methanol was excellently suitable for selective reduction of the C=C bond in a functionally substituted in the position *3* of 4,5,5-trimethyl-(or 5,5-pentamethylene)-2,5-dihydrofuran-2-one and 2*H*-pyran-2-one in the preparation of saturated lactones [13].

We applied the reducing system magnesium–methanol for selective reduction of the C=C bond in iminolactones **1a** and **1b** [1], where the C=C bond was conjugated with a carbamoyl substituent in the position C^3 of the iminolactone ring. The reduction of compounds **1a** and **1b** with the system magnesium–methanol afforded saturated lactones **2a** and **2b** in 85–88% yields. This reaction course apparently means that first the C=C bond is reduced, and further at the treatment of excess magnesium with diluted (1 : 1) hydrochloric acid the imino group suffers the hydrolysis with the formation of a lactone carbonyl. For the preparation of saturated iminolactones the excess magnesium was filtered off, and we obtained compounds **3a** and **3b** in 65 and 68% yields.



$R^1 = R^2 = CH_3$ (**a**); $R^1, R^2 = (CH_2)_5$ (**b**).

The structure of obtained compounds was established from the data of IR and ^{1}H NMR spectra. IR spectra of saturated iminolactones **3a** and **3b** lacked the band corresponding to the C=C bond of iminolactone ring in the region 1640–1660 cm^{-1}, and in the ^{1}H NMR spectra in contrast to the spectra of the initial compounds **1a** and **1b** signals of the protons H^3 and H^4 were present at 2.68 and 4.35 ppm. In the IR spectra of saturated lactones **2a** and **2b** the absorbance of the C=C bond in the region 1640–1660 cm^{-1} was also absent, and the absorption band appeared of the carbonyl group of the saturated lactone ring at 1760–1780 cm^{-1}. In the ^{1}H NMR spectra in contrast to the spectra of the initial compounds **1a** and **1b** signals were observed of protons H^3 and H^4 at 2.54 and 4.32 ppm.

The structure of compounds **2a** and **2b** was proved by a chemical reaction: the reduction of lactones **4a** and **4b** [14] by the system magnesium–methanol afforded compounds **2a** and **2b** in high yields (90–92%).

Saturated lactones 2a and 2b. *a*. A mixture of 0.01 mol of unsaturated iminolactone **1a** and **1b**, 2.4 g (0.1 mol) of magnesium turnings, and 50 mL of anhydrous methanol was stirred for 8–9 h at a room temperature. Excess magnesium was dissolved in diluted (1 : 1) hydrochloric acid, reaction products were extracted with ethyl ether, the extract was dried with magnesium sulfate, the solvent was evaporated, the residue was recrystallized.

b. A mixture of 0.01 mol of unsaturated lactone **4a** and **4b**, 2.4 g (0.1 mol) of magnesium turnings, and 50 mL of anhydrous methanol was stirred for 8–9 h at a room temperature. Excess magnesium was dissolved in diluted (1 : 1) hydrochloric acid, reaction products were extracted with ethyl ether, the extract was dried with magnesium sulfate, the solvent was evaporated, the residue was recrystallized from xylene.

4,5,5-Trimethyl-2-oxotetrahydrofuran-3-carboxamide (2a). Yield 1.5 g (88%) (*a*), 1.54 g (90%) (*b*), R_f 0.56, mp 92–93°C (from xylene). IR spectrum, ν, cm^{-1}: 3300 (NH), 1760 (C=O), 1680 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.18 d (3H, CH_3, *J* 7.0 Hz), 1.26 s (3H, CH_3), 1.45 s (3H, CH_3), 2.68 d.q (1H, CH, *J* 12.8, 7 Hz), 4.35 d (1H, CH, *J* 12.8 Hz), 7.23 br.s (1H) and 8.20 br.s (1H, NH_2).

4-Methyl-2-oxo-1-oxaspiro[4.5]decane-3-carboxamide (2b). Yield 1.8 g (85%) (*a*), 1.94 g (92%) (*b*), R_f 0.54, mp 147–149°C (from xylene). IR spectrum, ν, cm^{-1}: 3300 (NH), 1760 (C=O), 1680 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.19 d (3H, CH_3, *J* 7.0 Hz), 1.27 m (1H) and 1.58–1.82 m (7H, C_6H_{10}), 2.68 d.q (1H, CH, *J* 12.8, 7 Hz), 4.37 d (1H, CH, *J* 12.8 Hz), 7.23 br.s (1H) and 8.22 br.s (1H, NH_2).

A mixed sample of compounds **2a** and **2b** obtained by procedures *a* and *b* melts without depression of the melting point thus proving the identity of the compounds.

Saturated iminolactones 3a and 3b. A mixture of 0.01 mol of unsaturated iminolactone **1a** and **1b**, 2.4 g (0.1 mol) of magnesium turnings, and 50 m of anhydrous methanol was stirred for 8–9 h at a room temperature. Excess magnesium was filtered off, methanol was removed from the filtrate at a reduced pressure, the solid residue was recrystallized.

2-Imino-4,5,5-trimethyltetrahydrofuran-3-carboxamide (3a). Yield 1.10 g (65%), R_f 0.57, mp 126–128°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 3300 (NH), 3130 (NH), 1680 (C=O), 1640 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.15 d (3H, CH_3, *J* 7.0 Hz), 1.22 s (3H, CH_3), 1.44 s (3H, CH_3), 2.54 d.q (1H, CH, *J* 12.8, 7 Hz), 4.32 d (1H, CH, *J* 12.8 Hz), 7.21 br.s (1H, NH), 7.34 br.s (1H) and 8.26 br.s (1H, NH_2).

2-Imino-4-methyl-1-oxaspiro[4.5]decane-3-carboxamide (3b). Yield 1.43 g (68%), R_f 0.55, mp 180–182°C (from xylene). IR spectrum, ν, cm^{-1}: 3300 (NH), 3135 (NH), 1680 (C=O), 1640 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.15 d (3H, CH_3, *J* 7.0 Hz), 1.27 m (1H), 1.47 m (2H), 1.58–1.82 m (7H, C_6H_{10}), 2.54 d.q (1H, CH, *J* 12.8, 7 Hz), 4.32 d (1H, CH, *J* 12.8 Hz), 7.21 br.s (1H, NH), 7.36 br.s (1H) and 8.28 br.s (1H, NH_2).

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