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SHORT COMMUNICATIONS

New Preparation Procedure for *trans*-Imidodiols of Norbornane Series

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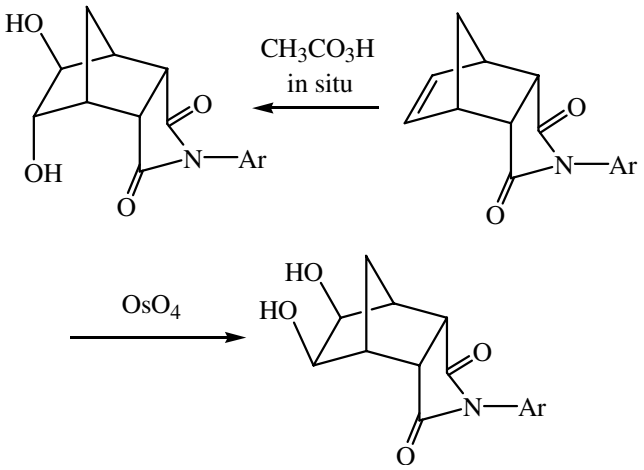
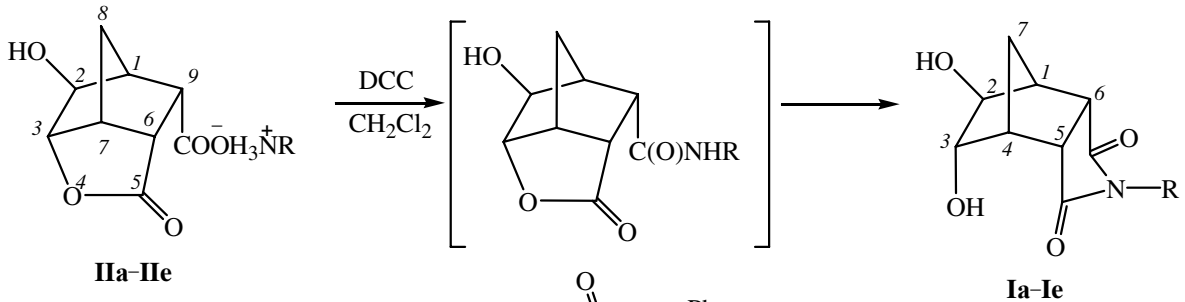
Several methods for synthesis of imidodiols of norbornene series were published. In [1, 2] the effect of the character of oxidant used on the stereochemistry of the oxidation process was demonstrated.



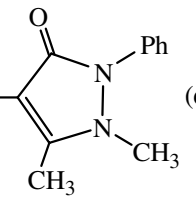
The goal of this study was a development of a new procedure for preparation of *trans*-imidodiols **Ia–Ie** by reaction of *exo*-2-hydroxy-5-oxo-*endo*-4-oxatricyclo-[4.2.1.$0^{3,7}$]nonane-*endo*-9-carboxylic acid salts **IIa–IIe** with dicyclohexylcarbodiimide (DCC).

Initial salts salts **IIa–IIe** were obtained either by epoxidation of amido acids (R = H, CH_2Ph) [3] or by reaction of equimolar amounts of *exo*-2-hydroxy-5-oxo-*endo*-4-oxatricyclo-[4.2.1.$0^{3,7}$]-nonane-*endo*-9-carboxylic acid with an appropriate amine at room temperature in a dichloromethane solution (salts **IIb, IId**, and **IIe**). In the latter case reaction of salts **IIb, IId**, and **IIe** with DCC was carried out as a "one-pot" synthesis without isolating salts in individual state.

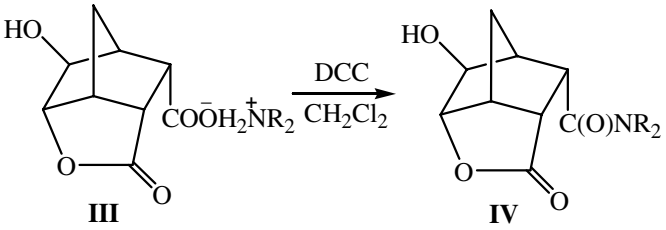
We showed formerly [3, 4] that under similar conditions the dehydration of salts of secondary amines **III** took an alternative route resulting in corresponding amidolactones **IV**.



IIa–IIe **Ia–Ie**

R = H (**a**), CH_3 (**b**), CH_2Ph (**c**),  (**d**), $C_6H_4CH_3$-*n* (**e**).

$NR_2 = N(C_2H_5)_2, N(C_5H_{11})_2, N(CH_2CH_2)_2O, N(CH_2)_6$.



III **IV**

The structure of compounds **Ia–Ie** synthesized was confirmed by IR and ^{1}H NMR spectra, and compound **Ib** was also subjected to X-ray diffraction analysis.

***trans*-Imidodiols Ia–Ie.** To 2 mmol of salt **IIa–IIe** in 10–12 ml of anhydrous dichloromethane was added at room temperature while stirring a solution of 0.41 g (2 mmol) of dicyclohexylcarbodiimide in 5 ml of dichloromethane. The reaction mixture was stirred for 5–10 days, the precipitate was filtered off and washed on the filter with duchloromethane. The filtrate was evaporated in a vacuum, the residue was ground under a layer of ethyl ether, the crystals thus obtained were filtered off, washed with ether, and dried in air. The precipitate was stirred with 12–15 ml of water for 40–60 min at 40–45°C, the insoluble in water dicyclohexylurea was filtered off and washed with water. The water filtrate was evaporated in a vacuum to dryness. Both portions of the reaction product were combined and repeatedly recrystallized from 2-propanol (or from acetone).

***exo*-2,*endo*-3-Dihydroxybicyclo-[2.2.1]-heptane-*endo*,*endo*-5,6-dicarboximide (Ia).** Yield 0.36 g (92.3%), mp 193–195°C, R_f 0.75 (2-propanol). IR spectrum, ν, cm^{-1}: 3440, 3345, 1755, 1680, 1580, 1405, 1205, 1068. ^{1}H NMR spectrum, δ, ppm: 7.38 s (1H, NH), 4.97 d (1H, OH^{endo}), 4.91 d (1H, OH^{exo}), 3.73 d (1H, H^3, $^3J_{3,4}$ 3.6 Hz), 3.21 s (1H, H^2), 3.09 d.d (1H, H^6), 2.87 d.d (1H, H^5, $^3J_{4,5}$ 5.1, $^3J_{5,6}$ 10.1 Hz), 2.60 m (1H, H^4), 2.31 d (1H, H^1, $^3J_{1,6}$ 5.7 Hz), 1.81 d (1H, H^{7syn}), 1.39 d (1H, H^{7anti}, $^2J_{7syn,7anti}$ 9.9 Hz). Found, %: C 54.73; H 5.71; N 7.12. $C_9H_{11}NO_4$. Calculated, %: C 54.82; H 5.62; N 7.10.

***N*-Methyl-*exo*-2,*endo*-3-dihydroxybicyclo-[2.2.1]heptane-*endo*,*endo*-5,6-dicarboximide (Ib).** Yield 0.32 g (76.3%), mp 184–186°C, R_f 0.60 (2-propanol). IR spectrum, ν, cm^{-1}: 3415, 3295, 1760, 1685, 1450. ^{1}H NMR spectrum, δ, ppm: 4.96 br.s (1H, OH^{endo}), 4.92 br.s (1H, OH^{exo}), 3.72 br.s (1H, H^3), 3.18 d.d (1H, H^6), 3.15 s (1H, H^2), 2.92 d.d (1H, H^5, $^3J_{4,5}$ 4.5, $^3J_{5,6}$ 9.5 Hz), 2.62 m (1H, H^4), 2.33 d (1H, H^1, $^3J_{1,6}$ 6.2 Hz), 1.83 d (1H, H^{7syn}), 1.43 d (1H, H^{7anti}, $^2J_{7syn,7anti}$ 10.4 Hz). Found, %: C 56.79; H 6.29; N 6.58. $C_{10}H_{13}NO_4$. Calculated, %: C 56.86; H 6.20; N 6.63.

***N*-Benzyl-*exo*-2,*endo*-3-dihydroxybicyclo-[2.2.1]heptane-*endo*,*endo*-5,6-dicarboximide (Ic).** Yield 0.51 g (88.5%), mp 127–130°C, R_f 0.12 (2-propanol). IR spectrum, ν, cm^{-1}: 3505, 3420, 1780, 1710, 1600, 1515, 785, 745, 715. ^{1}H NMR spectrum, δ, ppm: 7.30–7.23 (5H$_{arom}$), 5.09 br.s (1H, OH^{endo}), 4.99 br.s (1H, OH^{exo}), 4.51 d, 4.36 d (2H, CH$_2$, $^2J_{H,H}$ 14.9 Hz), 3.77 d (1H, H^3, $^3J_{3,4}$ 4.5 Hz), 3.27 d.d (1H, H^6), 3.21 s (1H, H^2), 3.02 d.d (1H, H^5, $^3J_{4,5}$ 4.7, $^3J_{5,6}$ 9.5 Hz), 2.65 m (1H, H^4), 2.35 d (1H, H^1, $^3J_{1,6}$ 5.8 Hz), 1.85 d (1H, H^{7syn}), 1.44 d (1H, H^{7anti}, $^2J_{7syn,7anti}$ 10.1 Hz). Found, %: C 66.81; H 5.89; N 4.91. $C_{16}H_{17}NO_4$. Calculated, %: C 66.89; H 5.96; N 4.88.

***N*-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)-*exo*-2,*endo*-3-dihydroxybicyclo-[2.2.1]heptane-*endo*,*endo*-5,6-dicarboximide (Id).** Yield 0.54 g (71.1%), mp 172–174°C, R_f 0.33 (2-propanol). IR spectrum, ν, cm^{-1}: 3450, 1788, 1725, 1680, 1605, 1510, 1400, 1195, 1060, 848, 785, 775, 725. ^{1}H NMR spectrum, δ, ppm: 7.54–7.47 (5H$_{arom}$), 5.14 br.s (1H, OH^{exo}), 5.07 d (1H, OH^{endo}), 3.83 br.s (1H, H^3), 3.42 d.d (1H, H^6), 3.39 s (1H, H^2), 3.16 s (3H, CH$_3$), 3.11 d.d (1H, H^5, $^3J_{4,5}$ 4.5, $^3J_{5,6}$ 9.9 Hz), 2.70 m (1H, H^4), 2.41 d (1H, H^1, $^3J_{1,6}$ 6.3 Hz), 2.21 s (3H, CH$_3$), 1.89 d (1H, H^{7syn}), 1.48 d (1H, H^{7anti}, $^2J_{7syn,7anti}$ 9.6 Hz). Found, %: C 62.72; H 5.44; N 11.01. $C_{20}H_{21}N_3O_5$. Calculated, %: C 62.65; H 5.52; N 10.96.

***N*-(4-Tolyl)-*exo*-2,*endo*-3-dihydroxybicyclo-[2.2.1]heptane-*endo*,*endo*-5,6-dicarboximide (Ie).** Yield 0.39 g (67.5%), mp 178–180°C, R_f 0.61 (2-propanol). IR spectrum, ν, cm^{-1}: 3520, 3455, 1762, 1695, 1522, 1400, 1195, 1050, 825. ^{1}H NMR spectrum, δ, ppm: 7.25 d (2H$_{arom}$), 7.11 d (2H$_{arom}$), 5.29 d (1H, OH^{endo}), 5.00 m (1H, OH^{exo}), 3.83 br.s (1H, H^3), 3.35 d.d (1H, H^6), 3.30 s (1H, H^2), 3.04 d.d (1H, H^5, $^3J_{4,5}$ 4.5, $^3J_{5,6}$ 9.8 Hz), 2.69 m (1H, H^4), 2.41 d (1H, H^1, $^3J_{1,6}$ 5.8 Hz), 2.33 s (3H, CH$_3$), 1.89 d (1H, H^{7syn}), 1.48 d (1H, H^{7anti}, $^2J_{7syn,7anti}$ 10.5 Hz). Found, %: C 66.96; H 5.99; N 4.97. $C_{16}H_{17}NO_4$. Calculated, %: C 66.89; H 5.96; N 4.88.

IR spectra were recorded on a spectrophotometer UR-20 in the region 4000–400 cm^{-1} from samples pelletized with potassium bromide. ^{1}H NMR spectra were registered on a spectrometer Varian VXR at operating frequency 300 MHz from solutions of compounds in DMSO-d_6, internal reference TMS. The reaction progress was monitored and the purity of compounds was checked by TLC on Silufol UV-254 plates, eluent 2-propanol, development in iodine vapor. Elemental analysis was carried out on an analyzer Carlo Erba.

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