steric hindrance of the *meso* form. In the future, we plan to study the reactivities of the compounds obtained in detail, the possibility of their synthesis, and the reactivities of the analogous *ansa*-metallocenes.

Experimental

X-ray diffraction study was performed on a CAD-4 diffractometer (Mo K_α radiation, graphite monochromator, $\theta \leq 27°$). The structures were solved by the heavy-atom method using the SHELX program based on 1885 (racemate) or 5022 (*meso*-form) reflections with $F > 4\sigma(F)$. Correction for absorption was applied using three azimuthal scan curves. The structures were refined anisotropically by the least-squares method with fixed positions of hydrogen atoms.

All synthesis procedures were carried out under a purified argon atmosphere *in vacuo* in Schlenk flasks. Solvents were purified by the standard procedures. $ZrCl_4$ (Reakhim) and 2,2′-bis[3-(triethyltin)indenyl]propane (GNIIKhTEOS) were used without additional purification.

The racemate and the *meso*-form of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride. A mixture of $ZrCl_4$ (4.60 g, 41.2 mmol) and 2,2-bis[3-(triethyltin)indenyl]propane (28.11 g, 41.2 mmol) in toluene (150 mL) was stirred at 80 °C for 3 h. Then the solvent was evaporated, and the residue was washed with hexane (2×50 mL) and dried. As a result, the equimolar mixture of the racemate and the *meso*-form of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride (according to the results of NMR) was obtained. The mixture was separated by fractional crystallization from CH_2Cl_2. Bright-orange crystals of the racemate (7.98 g, 45 %) and the *meso*-form (8.09 g, 45 %) of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride were obtained.

The racemate of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride forms monoclinic crystals (a = 15.903(9), b = 11.105(7), c = 11.520(9) Å, β = 121.61(4)°, Z = 4, space group $C2/c$, R = 0.0297, R_w = 0.0297); the corresponding *meso*-form gives triclinic crystals (a = 9.739(2), b = 12.798(4), c = 15.322(4) Å, α = 101.18(2), β = 121.61(4), g = 90.54(6)°, Z = 4, space group $P\bar{1}$, R = 0.0391, R_w = 0.0391).

The racemate of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride. Found (%): C, 58.27; H, 4.06. $C_{21}H_{18}Cl_2Zr$. Calculated (%): C, 58.32; H, 4.19. ^{1}H NMR (360 MHz; $CDCl_3$; δ): 2.34 (s, 6 H, $C(CH_3)_2$), 6.18 (d, 2 H, H(2) of the indenyl ligand), 6.65 (d, 2 H, H(3) of the indenyl ligand), 6.96—7.76 (m, 8 H, H(5,6,7,8) of the indenyl ligand).

The *meso* form of 2,2′-propylidene-bis(η^5-indenyl)zirconium dichloride. Found (%): C, 58.47; H, 4.23. $C_{21}H_{18}Cl_2Zr$. Calculated (%): C, 58.32; H, 4.19. ^{1}H NMR (360 MHz; $CDCl_3$; δ): 2.18 (s, 3 H, CH_3), 2.65 (s, 3 H, CH_3) 6.09 (d, 2 H, H(2) of the indenyl ligand), 6.67 (d, 2 H, H(3) of the indenyl ligand), 6.84—7.83 (m, 8 H, H(5,6,7,8) of the indenyl ligand).

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Preparation of *N*-nitrohydroxylamines by the substituting nitration method

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N-Nitro-*N*-methyl-*O*-substituted hydroxylamines were synthesized in high yields by nitration of appropriate *N*-acetylhydroxylamines with nitrogen pentoxide.

Key words: *N*-acetylhydroxylamines, nitration, *N*-nitrohydroxylamines, nitrogen pentoxide.

In the previous report,[1] for a number of examples we have shown that *N,O*-disubstituted *N*-nitrohydroxylamines (NHA) can be obtained by the sustituting nitration method from the corresponding *N*-acetylhydroxylamines (HA) by the action of nitronium salts and/or N_2O_5. In the present work, new possibilities and limita-

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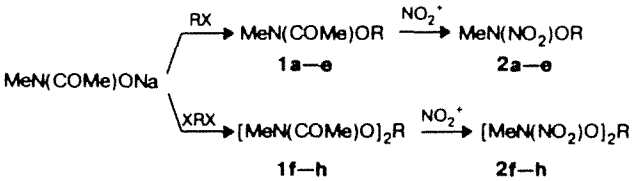
tions of this method are revealed.

N-acetyl-HA **1a—h**, prepared by alkylation of the Na salt of *N*-acetyl-*N*-Me-HA (AMHA) with the corresponding alkyl halides, were used as substrates for nitration.[1]



R = Me (**a**); Bu^n (**b**); C_8H_{17} (**c**); $MeOCH_2$ (**d**); $MeN(NO_2)CH_2$ (**e**); CH_2 (**f**); CH_2OCH_2 (**g**); $CH_2N(NO_2)CH_2$ (**h**)

Attempts to nitrate compounds **1e** and **1g** with $(NO_2)_2SiF_6$, as well as **1g** by treatment with NO_2BF_4, were unsuccessful. The nitration of compound **1e** with NO_2BF_4 followed by treatment of the reaction mixture with $NaHCO_3$ resulted in isolation of the corresponding NHA **2e** in *ca.* 40 % yield.

Since formation of Lewis acids (BF_3 and SiF_4) by decomposition of unstable acetyl derivatives of BF_4^- and SiF_6^{-2} in nitration with nitronium salts is possible, one can assume that these acids cause decomposition of the starting materials and/or the reaction products. In fact, it was shown by special experiments that compounds **1e**, **1g**, and **2e** decompose quite rapidly with BF_3 under conditions of nitration.

At the same time, nitration of compounds **1e** and **1g** by the action of N_2O_5 in MeCN at −25°C gives the corresponding NHA **2e** and **2g** in high yields. This reagent is effective in all cases, NHA **2c**, **2f**, and **2h** being isolated in *ca.* 90 % yields. Apparently, NHA **2a**, **2b**, and **2d** are also formed under these conditions, because with TLC monitoring, disappearance of the starting compound and formation of the new product are observed. However, these NHA are so volatile they cannot be isolated even from pentane, which was used for extraction of the reaction mixture.

The structure of products **2e—h** was confirmed by the elemental analysis, IR and ^{1}H NMR spectral data. The presence of two very strong bands of symmetric and antisymmetric stretchings of the $ONNO_2$ group at 1300 and 1600 cm^{-1} is the characterisic feature being general for all this compounds. Attempts to obtain elemental analysis data for product **2c** failed, because **2c** is rather labile even at +5 °C. This compound was characterized only by spectral data. The other isolated NHA are quite stable. Apparently, the thermal stability of NHA depends on electronegativity of the *O*-substituent, while electron-donating substituents decrease the stability of such compounds, as was assumed previously.[2]

Generalizing the above results and those reported in Ref. 1, one can conclude that the general method of synthesis of *N,O*-disubstituted NHA by substituting nitration of the corresponding *N*-acetyl-HA was elaborated. N_2O_5 is the most appropriate nitrating reagent. Using of nitronium salts is restricted by instability of the starting HA and the resulting NHA in the presence of Lewis acids, which are formed in these reactions. When nitronium salts are stable, their application is quite reasonable.[1]

Experimental

The IR spectra were registered in KBr tablets.

Preparation of Na salt of *N*-acetyl-*N*-methylhydroxylamine (AMHA). Equimolar amounts of *N,O*-diacetyl-*N*-Me-hydroxylamine[3] and MeONa in anhydrous methanol were stirred at 20 °C for 30 min; MeOH was removed, and the Na salt of AMHA (formed in quantitative yield) was used without further purification.

***N*-Acetyl-*N,O*-dimethylhydroxylamine (1a).** An equimolar amount of dimethyl sulfate was added to a solution of Na salt of AMHA in H_2O at cooling with ice-cold water and the mixture was stirred at 20 °C for 5 h, kept for 12 h, diluted with brine, and extracted with ether and the extract was dried over $MgSO_4$. After removal of ether, the residue was distilled to give **1a** (61 %), b.p. 80—81 °C (80 Torr), n_D^{20} 1.4228. Found (%): C, 46.51; H, 8.86; N, 13.40. $C_4H_9NO_2$. Calculated (%): C, 46.59; H, 8.80; N, 13.58. ^{1}H NMR ($CDCl_3$), δ: 1.95 (s, 3 H, Ac); 3.00 (s, 3 H, MeN); 3.60 (s, 3 H, MeO).

***N*-Acetyl-*N*-methyl-*O*-*n*-butylhydroxylamine (1b).** A 10 % excess of BuI was added to a dry Na salt of AMHA in anhydrous MeCN, and the mixture was stirred at 20 °C for 5 h and kept for 12 h; the solvent was removed, water was added to the residue, and the resulting solution was extracted with pentane and dried over $CaCl_2$. After removal of pentane, **1b** (73 %) was obtained by distillation, b.p. 69—70 °C (6 Torr), n_D^{20} 1.4310. Found (%): C, 57.76; H 10.11; N, 9.48. $C_7H_{15}NO_2$. Calculated (%): C, 57.90; H, 10.41; N, 9.65. ^{1}H NMR ($CDCl_3$), δ: 0.7—1.8 (m, 7 H, $Me(CH_2)_2$); 2.00 (s, 3 H, MeN); 2.06 (s, 3 H, Ac); 3.72 (t, 2 H, CH_2O).

Analogously, using *n*-OctI, chloromethyl ether (reaction time 1 h), and 1-chloro-2-nitrazapropane-3[4] or 1,1′-dichlorodimethyl ether and 1,3-dichloro-2-nitrazapropane-3,[4] *N*-acetyl-HA **1c—e,g,h** were obtained. For **1d,e,g,h**, the reaction mixtures were extracted with $CHCl_3$.

Compound **1c**, yield 85 %, b.p. 108—110 °C (1 Torr), n_D^{20} 1.4430. Found (%): C, 65.83; H, 11.35; N, 6.85. $C_{11}H_{23}NO_2$. Calculated (%): C, 65.63; H, 11.52; N, 6.96. ^{1}H NMR ($CDCl_3$), δ: 0.6—2.0 (m, 15 H, $(CH_2)_6CH_3$); 2.06 (s, 3 H, MeN); 2.12 (s, 3 H, Ac); 3.79 (t, 2 H, CH_2O).

Compound **1d**, yield 80 %, b.p. 78—80 °C (9 Torr), n_D^{20} 1.4341. Found (%): C, 45.24; H, 8.31; N, 10.48. $C_5H_{11}NO_3$. Calculated (%): C, 45.09; H, 8.33; N, 10.52. ^{1}H NMR (CCl_4), δ: 2.0 (s, 3 H, Ac); 3.13 (s, 3 H, MeN); 3.44 (s, 3 H, MeO); 4.82 (s, 2 H, CH_2).

Compound **1e**, yield 64 %, m.p. 50 °C (from ether). Found (%): C, 33.70; H, 6.18; N, 23.59. $C_5H_{11}N_3O_4$. Calculated (%): C, 33.88; H, 6.26; N, 23.72. ^{1}H NMR ($CDCl_3$), δ: 2.02 (s, 3 H, Ac); 3.16 (s, 3 H, MeN); 3.45 (s, 3 H, MeN); 5.41 (s, 2 H, CH_2).

Compound **1g**, yield 73 %, m.p. 90—92 °C (from ethyl acetate). Found (%): C, 43.45; H, 7.12; N, 12.84. $C_8H_{16}N_2O_5$. Calculated (%): C, 43.62; H, 7.32; N, 12.72. ^{1}H NMR ($CDCl_3$), δ: 2.08 (s, 3 H, Ac); 3.20 (s, 3 H, MeN); 5.11 (s, 4 H, 2 CH_2).

Compound **1h**, yield 67 %, oil, n_D^{20} 1.4846. The compound was purified by column chromatography (silica gel LC 100/160, eluent CH_2Cl_2). Found (%): C, 58.46; H, 9.81; N, 34.02. $C_8H_{16}N_4O_6$. Calculated (%): C, 58.54; H, 9.76; N, 34.15. ^{1}H NMR ($CDCl_3$), δ: 2.10 (s, 3 H, Ac); 3.24 (s, 3 H, MeN); 5.68 (s, 4 H, 2 CH_2).

Bis(*N*-acetyl-*N*-methyl-*O*-methylene)hydroxylamine (1f). Equimolar amounts of the Na salt of AMHA and CH_2I_2 were refluxed in anhydrous MeCN for 10 h, the precipitate was filtered off, the filtrate was evaporated, the residue was extracted with $CHCl_3$, and the oil formed was purified by preparative TLC (silica gel LC 5/40, eluent $CHCl_3$:EtOH, 10:1) to give **1f** (55 %), m.p. 42—44 °C. Found (%): C, 44.34; H, 7.32; N, 14.69. $C_7H_{14}N_2O_4$. Calculated (%): C, 44.19; H, 7.42; N, 14.73. ^{1}H NMR (CCl_4), δ: 2.02 (s, 3 H, Ac); 3.21 (s, 3 H, MeN); 5.28 (s, 2 H, CH_2).

***N*-Methyl-*N*-nitro-*O*-octylhydroxylamine (2c).** N_2O_5 (1.23 g, 11.4 mmol) was added to **1c** (2 g, 10 mmol) in 10 mL of anhydrous MeCN at −30 °C, the mixture was stirred at −20 °C for 40 min, the solvent was removed to a half of the volume, ice-cold H_2O (20 mL) was added, the mixture was extracted with pentane, the extract was dried over $CaCl_2$, pentane was removed and residue was purified by column chromatography (silica gel LC 100/160, eluent CH_2Cl_2) to give **2c** (1.65 g, 80.9 %) as a liquid. ^{1}H NMR ($CDCl_3$), δ: 0.6—1.8 (m, 15 H, $(CH_2)_6CH_3$); 3.33 (s, 3 H, MeN); 3.96 (t, 2 H, CH_2O). IR, ν/cm^{-1}: 1300, 1600 ($ONNO_2$).

***N*-Methyl-*N*-Nitro-*O*-2-nitrazapropylhydroxylamine (2e).**

a. NO_2BF_4 (0.35 g, 2.64 mmol) was added to **1e** (0.45 g, 2.54 mmol) in anhydrous MeCN (3 mL) at −25 °C; the mixture was stirred at −25 °C for 3 h, and $NaHCO_3$ (0.52 g) in H_2O (10 mL) was added; the mixture was extracted with CH_2Cl_2, and the extract was dried over $MgSO_4$. After removal of the solvent, **2e** (0.2 g, 43.5 %) was obtained as a liquid, which crystallized upon cooling, m.p. 55—56 °C (from Et_2O). Found (%): C, 19.86; H, 4.30; N, 30.95. $C_3H_8N_4O_5$. Calculated (%): C, 19.99; H, 4.48; N, 31.11. ^{1}H NMR ($CDCl_3$), δ: 3.40 (s, 3 H, MeN); 3.47 (s, 3 H, MeN); 5.63 (s, 2 H, CH_2). IR, ν/cm^{-1}: 1300, 1600 ($ONNO_2$); 1270, 1550 (NNO_2).

b. N_2O_5 (0.12 g, 1.11 mmol) was added to **1e** (0.18 g, 1.02 mmol) in anhydrous MeCN (2 mL) at −20 °C; the mixture was stirred at −15 °C for 15 min, the solvent was removed and **2e** (0.17 g, 94 %) was obtained, m.p. 55—56 °C.

***O,O''*-Methylene-bis(*N*-methyl-*N*-nitrohydroxylamine) (2f).** **1f** (0.80 g, 4.21 mmol) in anhydrous MeCN (4 mL) was added to N_2O_5 (0.91 g, 8.8 mmol) in anhydrous MeCN (3 mL) at −25 °C; the mixture was stirred at −20 °C for 2 h, the solvent was removed to a half of the volume, the mixture was diluted with H_2O, extracted with $CHCl_3$, and the extract was dried over $MgSO_4$. After removal of the solvents, the residual oil was purified on a column with silica gel LC 100/160 (eluent CH_2Cl_2) giving **2f** (0.81 g, 98 %), m.p. 31 °C. Found (%): C, 18.54; H, 4.03; N, 28.43. $C_3H_8N_4O_6$. Calculated (%): C, 18.36; H, 4.11; N, 28.57. ^{1}H NMR ($CDCl_3$), δ: 3.43 (s, 3 H, MeN); 5.49 (s, 2 H, CH_2). IR, ν/cm^{-1}: 1295, 1600 ($ONNO_2$).

***O,O'*-Oxopropylene-2-bis(*N*-methyl-*N*-nitrohydroxylamine) (2g).** **1g** (0.37 g, 1.68 mmol) in anhydrous MeCN (3 mL) was added to N_2O_5 (0.39 g, 3.61 mmol) at −35 °C; the mixture was stirred for 1 h at −25 °C, the solvent was removed, and the obtained crystals were washed with ice-cold H_2O and dried on air; **2g** was obtained (0.35 g, 92 %), m.p. 53 °C (from ether). Found (%): C, 21.33; H, 4.61; N, 24.70. $C_4H_{10}N_4O_7$. Calculated (%): C, 21.23; H, 4.46; N, 24.78. ^{1}H NMR ($CDCl_3$), δ: 3.47 (s, 3 H, MeN); 5.32 (s, 4 H, 2 CH_2). IR: ν/cm^{-1}: 1300, 1600 ($ONNO_2$).

***O,O'*-2-Nitrazapropylene-bis(*N*-methyl-*N*-nitrohydroxylamine) (2h).** A solution of **1h** (0.38 g, 1.44 mmol) in anhydrous MeCN (0.5 mL) was added to N_2O_5 (0.32 g, 3 mmol) in anhydrous MeCN (1 mL) at −35 °C; the mixture was stirred at −25 °C for 1 h, the solvent was removed, and the obtained crystals were washed with H_2O and dried on air; **2h** (0.36 g, 93 %) was obtained, m.p. 63—65 °C. Found (%): C, 17.83; H, 3.79; N, 30.94. $C_4H_{10}N_6O_8$. Calculated (%): C, 17.77; H, 3.73; N 31.11. ^{1}H NMR ($CDCl_3$), δ: 3.39 (s, 3 H, MeN); 5.66 (s, 2 H, CH_2).

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