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SHORT COMMUNICATIONS

Synthesis of Aliphatic Hydroxyethyl-Substituted Ureas

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Hydroxyalkyl-substituted ureas are polyfunctional organic compounds that are widely used in the chemistry of high-molecular-weight compounds [1–5]. For example, tetrakis(hydroxyethyl)-substituted ureas were used to modify epoxy and urethane polymers with the goal of improving their performance [3–5]. Ureas derived from hexane-1,6-diyl diisocyanate turned out to be the best modifiers due to low melting points and good compatibility with epoxy [3] and urethane oligomers [4, 5]. Taking the above stated into account, in the present work we synthesized polymethylene-bridged hydroxyethyl-substituted bis-ureas **3a** and **3b**. Octane- and decanedioic acids were treated with phosphorus trichloride to obtain dichlorides **1a** and **1b** which were converted into diisocyanates **2a** and **2b** via Curtius rearrangement of the corresponding azides (through acylnitrenes) [6]. Diisocyanates **2a** and **2b** reacted with bis(2-hydroxyethyl)amine to afford desired bis-ureas **3a** and **3b**.

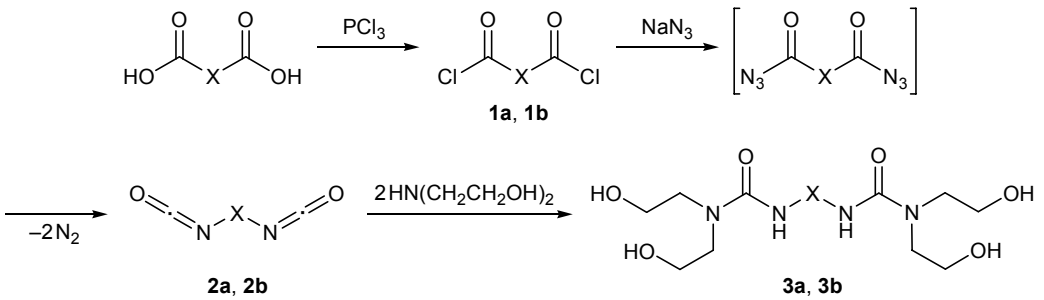
After recrystallization from ethanol, compounds **3a** and **3b** were isolated as colorless crystalline substances readily soluble in water at room temperature and in ethanol, butan-1-ol, and DMF on heating and insoluble in diethyl ether, benzene, and carbon tetrachloride. Their structure and purity were confirmed by elemental analyses, IR and ^{1}H NMR spectra, and TLC data.

Octane- and decanedioyl dichlorides **1a** and **1b** were prepared according to the procedure described in [7]. Colorless transparent liquids; **1a**: bp 168°C (18 mm), d_4^{20} = 1.1240, n_D^{20} = 1.4672; **1b**: bp 163°C (20 mm), d_4^{20} = 1.1145, n_D^{20} = 1.4542.

Octane-1,8-diyl diisocyanate (**2a**) and decane-1,10-diyl diisocyanate (**2b**) were synthesized as described in [8]. Colorless transparent liquids; **2a**: bp 165–167°C (20 mm), d_4^{20} = 1.0189, n_D^{20} = 1.4521; published data [9]: bp 156°C (15 mm), d_4^{20} = 1.007, n_D^{20} = 1.4550; **2b**: bp 183–185°C (20 mm), d_4^{20} = 0.9988, n_D^{20} = 1.4654; published data [9]: bp 154–157 (5 mm).

Compounds **3a** and **3b** were synthesized as described in [9].

3,3′-(Octane-1,8-diyl)bis[1,1-bis(2-hydroxyethyl)urea] (3a). Yield 87%, mp 56–58°C, R_f 0.65. IR spectrum, ν, cm^{-1}: 3300, 3220, 3075 (NH, OH), 2910, 2900, 2820, 1465 770–720 (CH_2), 1620, 1580, 1265 (CO, NH). ^{1}H NMR spectrum, δ, ppm: 1.30 m (8H, CH_2), 1.54 m (4H, CH_2), 3.10 t (4H, CH_2, ^3J = 6 Hz), 3.30 t (4H, CH_2N, ^3J = 6 Hz), 4.00 m (6H, CH_2O, OH),



X = $(CH_2)_8$ (**a**), $(CH_2)_{10}$ (**b**).

8.05 s (2H, NH). Found, %: C 53.01; H 8.27; N 13.60. $C_{18}H_{36}N_4O_6$. Calculated, %: C 53.45; H 8.96; N 13.85.

3,3′-(Decane-1,10-diyl)bis[1,1-bis(2-hydroxyethyl)urea] (3b). Yield 90%, mp 44–46°C, R_f 0.71. IR spectrum, ν cm^{-1}: 3285, 3210, 3065 (NH, OH), 2920, 2810, 1467, 770–720 (CH_2), 1620, 1580, 1265 (CO, NH). ^{1}H NMR spectrum, δ, ppm: 1.30 m (12H, CH_2), 1.54 m (4H, CH_2), 3.12 t (2H, CH_2, ^3J = 6 Hz), 3.30 t (4H, CH_2N, ^3J = 6 Hz), 4.05 m (6H, CH_2O, OH), 8.00 s (2H, NH). Found, %: C 55.87; H 9.27; N 12.68. $C_{20}H_{40}N_4O_6$. Calculated, %: C 55.54; H 9.31; N 12.95.

The IR spectra were recorded on an FSM 1202 spectrometer from thin films. The ^{1}H NMR spectra were measured on a Bruker DRX500 spectrometer (500.13 MHz) from solutions in DMSO-d_6 using tetramethylsilane as internal reference. Analytical thin-layer chromatography was performed on Sorbfil PTSKh-P-V plates using ethanol–hexane (3 : 1) as eluent and iodine vapor as developer. The elemental analyses were obtained on a Perkin Elmer 2400 CHN analyzer.

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